ANNUAL REVIEW NUMBER

The Chemical Age

VOL LXVI 12 JANUARY 1952 No 1696

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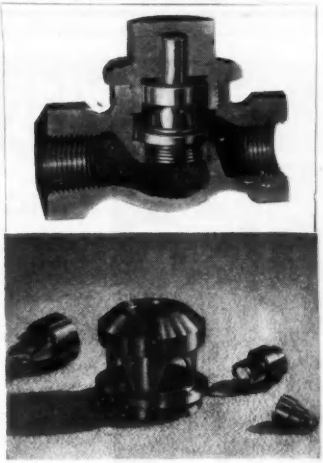

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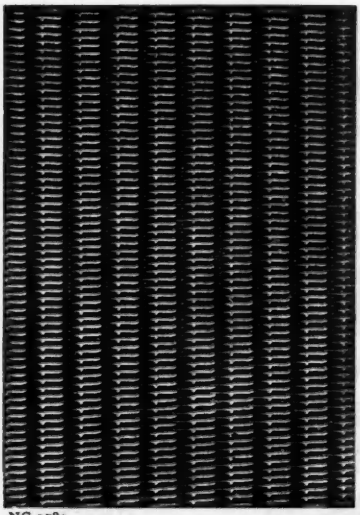

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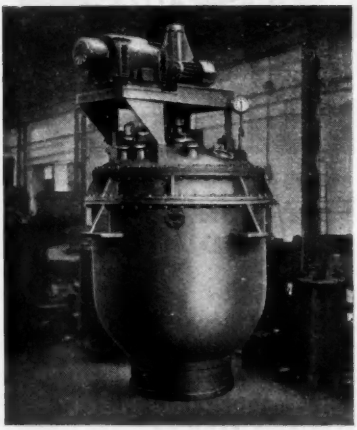

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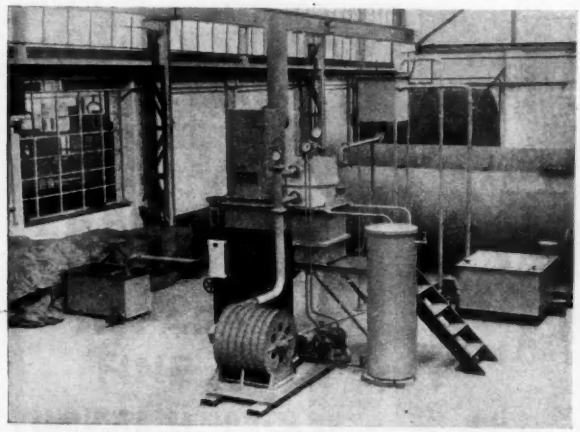

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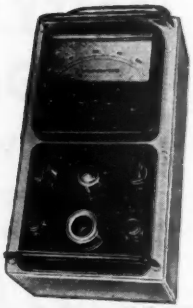

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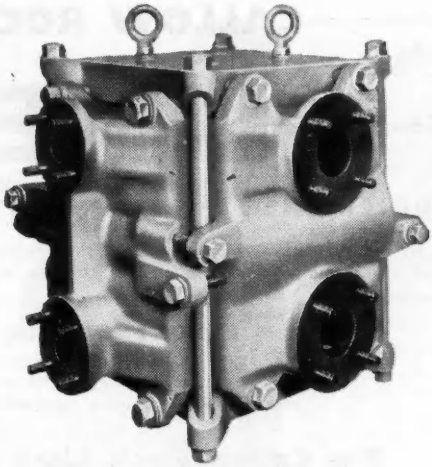

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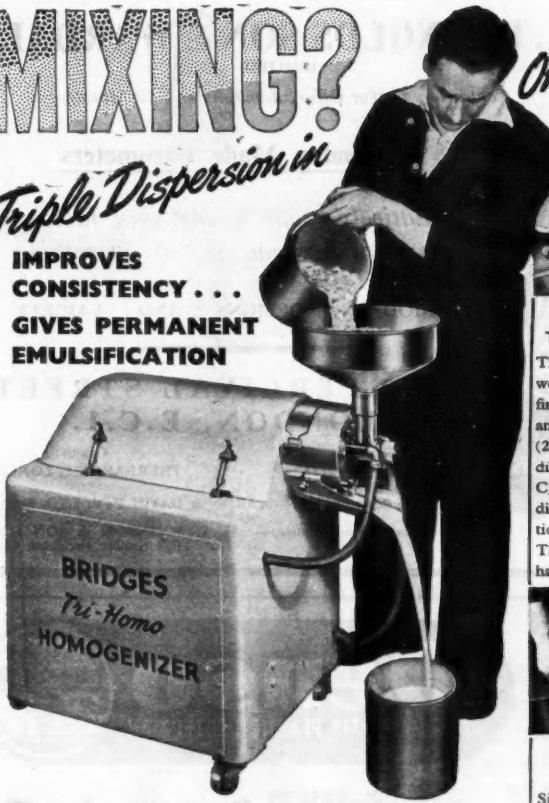

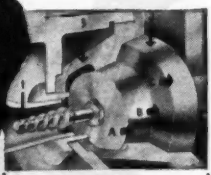

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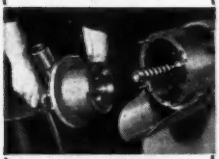

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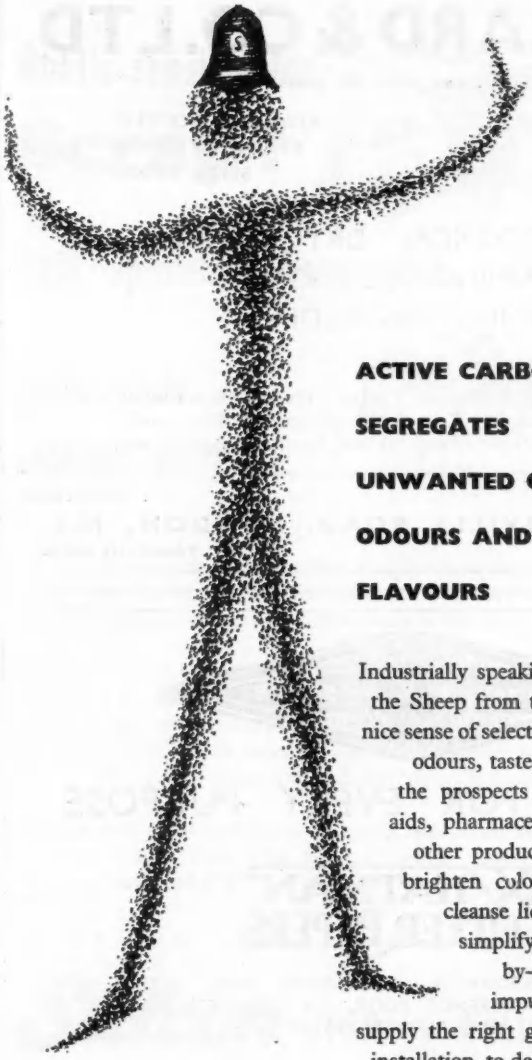

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The Second Half

WE no longer stand on the threshold of the twentieth century's second half. We have entered into it, have endured its first perplexed twelve months. For Britain it was pre-planned as a year of festival but even the stoutest-hearted enthusiasts for the South Bank and Battersea's gardens must admit that the Festival, however efficiently organised, had a somewhat carbonated effervescence rather than the natural ebullition of national celebration. The world of 1951 is vastly different from the world of 1851, far less certain of future security, far less readily impressed by miracles of material ingenuity. Looking back upon the lately departed year of 1951, it is not unfair to say that one of the things we shall not remember indelibly is that it was Festival Year. Political changes, both at home and internationally, are likely to prove much more memorable. By a hairsbreadth shift in British electoral opinion, we have seen Mr. Attlee's team depart and Mr. Churchill's team arrive. Internationally the deadlock of the cold war between East and West has continued to waste away the present and the future, locking up huge proportions of valuable materials and mortgaging the prospects of better standards of living. Yet there was in the last few weeks of the year a faint sign—all too faint perhaps but better than nothing—of easing tension. We may realise in 1955 or 1956 that 1951 was in fact a year of turning-point.

For the chemical industry 1951 was a year of increasing difficulty, mainly because the problem of sulphur and sulphuric acid supplies hung like a darkening cloud over so many branches of the industry. Effort and capital that might otherwise have been devoted to further expansion have had to be allocated to projects for replacing imported American sulphur, projects that will not provide appreciable relief until 1953 or even later. At least the challenge of the sulphur crisis has been faced boldly. Nor need we regard it bitterly as a raw material crisis induced by the world's political uncertainty—Korea and rearmament have merely hastened the problem of sulphur scarcity and we may yet be glad that we were forced to grapple with it in 1951 instead of continuing to ignore the reckless danger of basing so much of our chemical industry upon the dwindling reserves of Gulf Coast sulphur.

The bleakest section of the chemical industry, at any rate at the end of 1951, was that of fertiliser manufacture. Severe advances in prices followed the removal of subsidies in the mid-year and at a time when further expansion in our production of food at home was never more vital in peace the demand for fertilisers dropped disastrously. In most other countries fertiliser consumption is continuing to expand steadily, held back only by the shortage of sulphuric acid to treat rock phosphate. The ability of the British farmer to purchase fertilisers now depends on economic considerations. Here again, however, 1951 may have ended with signs of a turning-point in crisis. The restoration of a subsidy scheme for phosphatic fertilisers was at least an emergency step in the right direction. At the same time costs of fertiliser manufacture are steadily rising and the only prospect for the future is that fertilisers must become dearer rather than cheaper. There are few products of the chemical industry of which it may be said more accurately that so much is produced by so little.

The ability of chemists and chemical substances to increase food productivity seems likely to be their dominant responsibility in the second-half of the century. Progress in this direction has not been inadequate in 1951. In America the use of antibiotics as trace supplements in feeding-stuffs has spectacularly increased the growth-rates of poultry and pigs; and a new rodenticide—warfarin—has completed its first full year of general use with a record of success that may well revolutionise man's constant food war with rats. It is almost ironic that the same period in history has seen an intensification of popular and not too well-informed attacks upon the use of chemicals in food production and food processing. No doubt this is an expectable reaction from the expanding use of chemicals; as a form of vigilant control for incautious uses these criticisms must be welcomed but 1951 has shown that immoderate extremism attracts far more attention than balanced and constructive questioning.

In almost the last minutes of the year a new advance in agricultural science was made known. A substance called krilium is said to be able to 'rejuvenate' barren soils. In the newspaper press we have been told that even deserts will bloom again with the aid of krilium. The prudent reader will adopt Asquith's famous advice to wait and see. Indeed, Krilium might well be dismissed as a headline fantasy were it not for the fact that one of the principal chemical corporations of the United States is reported to be investing fifty million dollars in plant for its large-scale production. Should these hopes prove justified, the discovery of this substance will outshine all other achievements of the beginning of the twentieth century's second half.

On Other Pages

The annual subscription to THE CHEMICAL AGE is 35s. Single copies, 9d.; post paid, 1s.; SCOTTISH OFFICE: 116 Hope Street, Glasgow (Central 3954/5). MIDLANDS OFFICE: Daimler House, Paradise Street, Birmingham (Midland 0784-5). THE CHEMICAL AGE offices are closed on Saturdays in accordance with the adoption of the five-day week by Benn Brothers, Limited.

Notes & Comments

1952 Anniversaries

A NEW year always brings notable anniversaries and 1952 is no exception. It is the centenary of the birth of one of the greatest British chemists of all time—Sir William Ramsay. The University of London has had many brilliant occupants of its Chairs of chemistry but few would deny that Ramsay still outshines them all. Another Nobel Prize winner born in 1852 was Professor Moissan of Paris, perhaps best known for his studies of fluorine compounds and the isolation of fluorine in the 'eighties. Another birth-centenary to be recognised this year is that of Emil Fischer, Professor at Berlin and one of the truly great pioneers of modern organic chemistry. It is an unusual coincidence that three such great men of chemistry should have been born in the same year and all made their contributions to chemistry in the principal capitals of Europe—London, Paris, Berlin. As for chemical events of 1852, perhaps the most notable was Williamson's theory on the formation of ethers. Some chemical historians also credit 1852 with Frankland's discovery of the organometallic compounds but it is probably more accurate to say that 1852 was only one year of several during which this work reached its first climax. Looking forward, however, there is this year an outstanding jubilee to celebrate; fifty years ago Madame Curie isolated radium salts. We seem to have made a vast and (in the eyes of the layman at least) dangerous journey along the radioactive road since 1902.

A Publishing Venture

MEMBERS of the Society of Chemical Industry will recently have received a new publication, a supplement to *Chemistry and Industry*, containing all the papers on 'Water and Industry' read at the Society's annual general meeting this summer. Formerly papers read at these meetings have been separately published as and when space could be found in the normal journals. Few will deny that it is far better for the principle of collectivity to apply to print as well as platform. It has always been regrettable that scattered and piecemeal publication should follow the oral symposium of a 'subject' conference. This new venture by one of our major scientific organisations might well be the model for others for in recent years the symposium or conference method of paper presentation and subject discussion has grown steadily. Unfortunately the paper situation and the economics of publishing are dictating contraction rather than expansion, and the excellence of 'Water in Industry' may prove to be no more than a bitter-sweet sample of publishing possibilities.

Chemical Expansion

ACHIEVEMENTS of the British chemical industry in 1951, despite raw material shortages and other problems, are something of which it may be justifiably proud. Overseas trade during the first 10 months of last year rose by £31,000,000 over the same period of 1950, to a total of £118,000,000 which included big increases in exports to the U.S.A. and Canada. This record was attained, as was pointed out by Mr. T. C. Fawcett, chairman of the chemical and allied trades section of the Manchester Chamber of Commerce at its annual general meeting, only by the combined efforts of chemical manufacturers, distributors and users. At the same time, he warned that stronger competition in world markets from Germany and Japan must be expected in future. No doubt an important factor which has enabled the British chemical industry to maintain its prominent position was the planning of long-term projects, a number of which are now beginning to prove effective while others are still approaching completion. Capital expenditure has, indeed, been remarkable; that for mineral oil refining rose from £6,000,000 in 1948 to £32,000,000 in 1950, while other chemical and allied trades increased from £39,000,000 in 1948, to £61,000,000 in 1950.

Rebuilding Europe's Chemical Industry

Wide Range of ECA Assistance

WHEN the Marshall Plan tackled its work of relief and rebuilding in Europe in the spring of 1948, one of the industries hardest hit by the war was chemicals. Germany, which had been the chemical heart of Europe, was desperately crippled, and the industry in some other countries was hurt nearly as badly.

Stepped into Breach

The Marshall Plan stepped into the breach by bringing in a quarter of a billion dollars worth of American chemicals, mostly raw materials which were the basis for finished products worth billions. These basic imports included $50,000,000 of medicinal and chemical preparations; $46,000,000 of pigments and other paint materials; $4,000,000 of insecticides for the control of health or crop pests, and $150,000,000 of general and industrial chemicals and alcohol.

In addition to aid for chemicals as such, the petroleum and coal-refining industries have received Marshall Plan aid to a total of about $550,000,000. Some of this has been in direct dollar aid and the rest has been in 'counterpart funds'—funds which the Marshall Plan countries have accumulated in their own currencies by selling to their own citizens Marshall Plan raw materials, such as wheat, cotton, crude oil and machinery.

Apart from raw materials, many chemical plants have received dollar aid for the purchase of machinery not readily obtainable, or not obtainable at all—in Europe. Such aid has ranged from a few thousand dollars into the millions.

At Grangemouth on the East Coast of Scotland, British Petroleum Chemicals, Ltd., is erecting a $17,000,000 plant to manufacture intermediate chemicals—ethyl, *iso*propyl and butyl alcohols, styrene, ethylene oxide derivatives and so on—from the by-products of an already existing oil-refining plant. The ECA's contribution will be $6,500,000. For a similar plant being built near Marseilles by the Société Naphta-Chimie, the ECA is advancing $1,700,000 of the total cost of $12,500,000. At Ferrara, Italy, on the Adriatic, Montecatini, 'the Dupont Corporation of Italy,' is building yet another plant to manufacture more chemicals from petroleum. The total cost here will be $18,700,000, with the ECA advancing $2,670,000.

The most important development in phosphates has been the modernising and enlarging of the phosphate rock mines in French North Africa. These improvements have cost well over $100,000,000, about one-tenth coming from Marshall Plan funds.

In French Alsace some $125,000,000 has been spent to bring up-to-date and enlarge the potash mines, by far the most important single source of potash for Western Europe.

Production of nitrogenous fertilisers has mounted steadily since the end of the war. The Marshall Plan has set aside $4,500,000 toward the construction of an ammonium sulphate plant in Italy. Iceland has been awarded about $2,580,000 toward the total $6,700,000 for a nitrogen plant which will use the year-round supply of water-power to produce fertilisers for consumption in Iceland.

Probably the most closely-watched chemical of all—because it is one of the most essential as well as one of the scarcest—has been sulphur. To increase the supply available for Western Europe the U.S.A. has controlled the consumption of sulphur at home and has controlled the price both at home and for export. During the last year sulphur prices rose less than 15 per cent against a 100 per cent rise for tin and a 300 per cent increase for rubber.

Pyrites Mining Encouraged

Before the scarcity of sulphur became so acute production of sulphur from pyrites in Europe was hardly an economic proposition as the method cost about twice the price of imported American sulphur. With the reduction of exports from the U.S.A. since the beginning of 1951, mining of more pyrites to augment the sulphur supply has become important and ECA has aided this development.

Expansion of Europe's own chemical industry, and of the allied oil-refining industry, has made Europe independent of American chemicals in many lines. This trend will strengthen as the new plants now under construction are completed.

The DSIR in 1951

Conservation Methods Receive Special Attention

AN outstanding feature of the research programme for 1951 was the attention accorded to the conservation of scarce materials, notably sulphur, by the development of acceptable substitutes, more economical manufacturing processes, or improved methods of recovery. Much of this work was started some years ago, so that the Department of Scientific and Industrial Research was able to render prompt assistance in alleviating the emergencies which arose, besides proceeding with investigations of a more long-term nature.

The DSIR acted as scientific advisers to the Ministry of Materials and officers of the department sat on the Ministry's Committees. Although the Natural Resources (Technical) Committee is a committee of the Lord President's Office, members of the department serve on the main committee and on its working parties. The subjects dealt with included sulphur, utilisation of straw, raw materials for synthetic fibres, mineral resources, agriculture, timber, fish waste, and iron ore supplies.

Under OEEC there is a Committee for Scientific and Technical Matters with Dr. Alexander King, head of the DSIR's Intelligence Division, as the chairman. The Committee has a Sub-Committee for Co-operation in Scientific Research and Technical Development. This Sub-Committee has set up a number of working parties, one of which is studying economy of sulphuric acid in the manufacture of phosphate fertilisers. The working party includes three United Kingdom representatives, who are seconded by the Ministry of Agriculture, the Agricultural Research Council and the DSIR. Mr. A. L. Thorogood, of the DSIR, is Technical Secretary. The chairman is M. Massenet, who is Director-General of Potasse et Engrais Chimiques. Two meetings were held in Paris and a third was scheduled to take place at the beginning of January this year.

Phosphate Fertilisers

A paper by DSIR giving an account of phosphate fertilisers which economise in sulphuric acid was sent to Western European countries. Other countries have added to this report, and now each country is preparing answers to a questionnaire sent by the working party regarding the fertilisers produced by their own manufacturers. These include high temperature fusion processes, processes employing nitric acid, products made by fusion with alkalis, superphosphates, dicalcium phosphate processes, ground phosphate rock and basic slag. Sample quantities of fertilisers used abroad have been imported to Britain and field trials are being carried out to study the response under United Kingdom conditions. It is hoped that this co-operative research between Western European countries will result in the development of new processes and techniques.

The Chemical Research Laboratory examined alternative methods of making phosphate fertilisers, the most attractive possibility being to use nitric acid instead of sulphuric acid. A method was successfully developed for treating rock phosphate with a mixture of nitric acid and sulphuric acid

Dr. A. King, head of the Intelligence Division, DSIR, speaking at the International Symposium on the organisation of scientific and industrial research

in the proportion of about 4 to 3. This process gives a product which is relatively non-caking and will keep reasonably dry in the normal British climate. Experiments were also carried out to produce a 'complete' fertiliser by adding potassium chloride, the chief source of potash. An N-P-K fertiliser containing 10 per cent of potash was prepared and is likely to prove a reasonably good product in practice.

Collaborative research by the DSIR and the Agricultural Research Council showed that certain tar oils might be useful substitutes for sulphuric acid for potato haulm destruction, a purpose for which over 10,000 tons of acid a year are used. Some of the substitutes developed have already been used on a substantial scale.

The Fuel Research Station continued its work on the production of ammonium sulphate from power station flue gases, using the Fulham Simon-Carves process, which was tried in preliminary tests before the war in a pilot plant at the Fulham generating station. The results obtained from a small pilot plant scrubber at the Fuel Research Station proved so promising that a plant capable of washing 2,000 cu. ft. of gas per hour and producing ammonium sulphate has been installed.

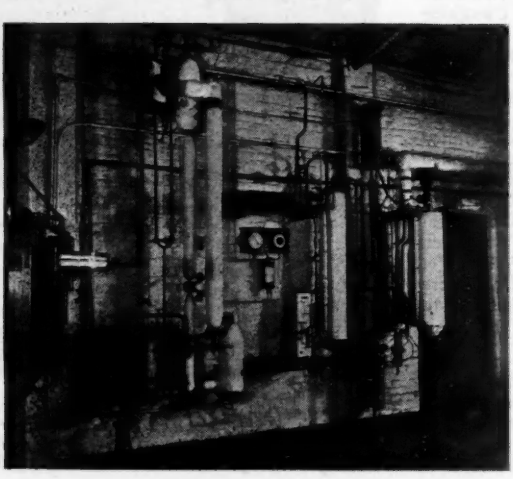
Attention has also been directed to the recovery of sulphur from unpurified coke oven gas. About 20,000 tons of sulphur could be recovered annually from the ten largest coke ovens and a programme is under way to install iron oxide boxes or other recovery equipment.

In 1950, two scientists from the Chemical Research Laboratory surveyed certain desert lakes in Libya, which are full of sulphate-reducing and sulphide oxidising bacteria. These micro-organisms reduce sulphates to sulphides and finally to sulphur. The rate of production of sulphide is low, and to make the process economically feasible it would be necessary to speed up the reduction of sulphates to about ten times its normal rate. This possibility is being investigated at the CRL.

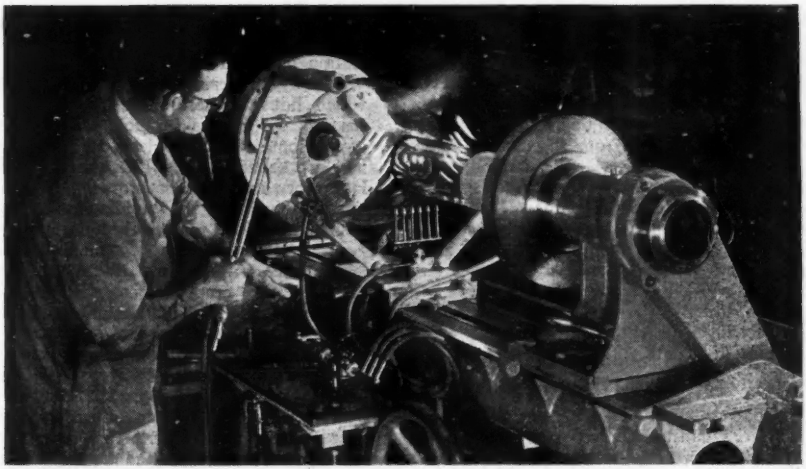
The titanium dioxide industry in Britain uses large quantities of sulphuric acid for dissolving ilmenite, the waste acid including thousands of tons of copperas. Recent work encouraged by DSIR has found potential uses for this product in the gas industry.

The rayon industry uses sulphur in the form of CS_2 for dissolving cellulose and in the form of H_2SO_4 in spinning baths. Yet sulphur does not enter into the end product. Research is therefore in progress to recover CS_2 from the air in the factory and also sulphuric acid in the form of sodium sulphate from the spinning baths.

A survey was carried out during the year of the use of aluminium sulphate in water treatment and in the paper industry. Each of the water boards is carrying out its own experimental work in this direction. In the paper industry it is technically possible to use chemicals which contain no sulphur, but



Plant for the synthesis of methane using a converter with a moving bed of catalyst at the fuel research station at Greenwich. During the year the DSIR published a report of the work done at the station during the years 1946-49



Glassworking lathe in horizontal position at the Chemical Research Laboratory

these are not available at present and the cost is very high. There is a possibility of using waste aluminium chloride as a partial replacement, but the quantity potentially available is very small in comparison with the total use.

Thousands of tons of sulphuric acid are consumed annually in the surface treatment of steel by sulphuric acid pickling. An autoxidation process for the regeneration of sulphuric acid from ferrous sulphate in waste pickle liquors was developed by BISRA and will be tested in a pilot plant being erected at a steel works in South Wales. There are two kinds of waste pickle liquors, containing respectively hydrochloric acid and sulphuric acid, both of which might be used to replace aluminium sulphate in water treatment should the need arise. Cost would be governed largely by transport, but this field of research appears to present interesting possibilities for water treatment plants situated near steel works.

Work on the conservation and recovery of other scarce materials was carried out during the year by various research organisations. The British Non-Ferrous Metals Research Association and BISRA are both working on the conservation of zinc in galvanising, while the recovery of zinc from plating solutions is one of the practical applications of ion exchange resins being investigated by the CRL.

Workers at the Fuel Research Station investigated two possible methods of improving the conventional Fischer-Tropsch process, namely the use of a fluid bed for the reactions and by using a catalyst in oil. Not enough work has been done on either process to warrant an assessment of the economic possibilities, but a large-scale plant for the liquid-phase slurry process was constructed during the year and is expected to yield much valuable chemical engineering information. Further work was also carried out on the production of water gas.

The more economical use of solid fuel in homes and factories remained one of the major research targets of the Fuel Research Station, BCURA and other organisations associated with this work.

Good progress was made during the year with experimental studies at the Pest Infestation Laboratory, in which radioactive isotopes are being used to trace the distribution of insecticides inside the insects to which they have been applied, and also to determine the nature and ultimate fate of insecticide residues contaminating food. Evidence so far obtained indicates that resistant flies are able to convert DDT into a non-toxic compound, while susceptible flies cannot do so. Techniques developed for these studies were described.

'Neolite' is an American trade name for a variety of resin-rubber used as a substitute

for sole leather. It is based on a copolymer of butadiene and styrene and by varying the proportions of the monomers the properties of the product can be varied. This material is claimed to have all the good qualities of leather and to wear up to five times as long. Samples were sent from the United Kingdom Scientific Mission in Washington by the courtsey of American manufacturers to the British Boot, Shoe and Allied Trades Research Association for investigation. A number of British manufacturers are interested and have developed types of resin-rubber of their own, which are expected to be on the British market this year. This project links up with the new production of styrene in Britain.

Mechanical Engineering

Good progress was made during the year with the construction of new laboratories and workshops for the Mechanical Engineering Research Organisation at East Kilbride in Scotland. The first buildings completed at East Kilbride were the workshop, the boiler house, and the main part of the Properties of Materials laboratory. So that the most rapid progress can be made with research, the laboratory will be used at first as a general purpose building available for experimental work on materials, mechanics of solids, fluid flow, heat transfer and mechanics of formation. The headquarters of the organisation, together with the Lubrication Division, the Machine Shaping Section and parts of the Mechanisms and Formation Section, have been at Thorntonhall, Glasgow, for some time. Much of the work formerly done in the Engineering Division of the National Physical Laboratory was transferred to East Kilbride in June. This move involved the transport to Scotland of about 120 tons of machines and scientific equipment. The sections of MERO working on fluid mechanics and mechanics of formation were transferred from the NPL to Scotland during August.

Dr. D. G. Sopwith, D.Sc., M.I.Mech.E., was appointed Director of Mechanical Engineering Research. He was formerly superintendent of Engineering Division of NPL and since the death of Dr. G. A. Hankins in November, 1950, he had been Acting Director of Mechanical Engineering Research.

On 24 May the Rt. Hon. Sir John Anderson, G.C.B., G.C.S.I., G.C.I.E., opened the new laboratory of the British Hydromechanics Research Association at Harlow, Essex. The British Baking Industries Research Association extended their premises at Chorley Wood by the erection of a new building which houses laboratories for research in baking. As a base for field teams investigating some of the problems of iron-making and ore beneficiation, BISRA set up a new laboratory near Middlesbrough. Its activities also included the building of a group of metal working, chemical engineering and general laboratories at Sheffield. These laboratories will increase the Association's facilities for practical research on steel-making, metal working, metallurgy, corrosion and analytical chemistry.

Among the most important scientific events of the year was a conference on Automatic Control, which opened on 16 July at the Royal College of Aeronautics, Cranfield, near Bedford. This conference was organised by the DSIR, with the support and co-operation of the Institution of Electrical Engineers and the Institution of Mechanical Engineers, in order to discuss and advance the development of automatic and manual control systems. It was attended by over 300 engineers, scientists and mathematicians, most of the leading industrial countries in the world being represented.

Building Research Congress

Another outstanding event was the first international Building Research Congress, which was held in London from 11-20 September, arrangements for the Congress being in the hands of the Building Research Station. Some 1,500 members participated and delegates were present from 55 countries, including Austria, Finland and Japan. Nearly ninety papers were presented, and six large halls were barely sufficient to accommodate all those taking part in the various sessions.

About 130 delegates from the iron, steel and other interested industries attended a conference organised by BISRA and held on 3 and 4 October at Leamington Spa. Standardisation proposals for the spectrographic analysis of the alloying elements in steel were discussed. A number of papers were presented, most of which dealt with the determination of gases or metals in alloy steels. Another conference was devoted to immersion pyrometry and the use of the oxygen lance.

The DSIR was represented on Mission 81.

Financed by OEEC, this mission consisted of an international team which visited various European countries to study the organisation and use of applied research. This investigation culminated in an International Symposium on the Organisation of Scientific and Industrial Research. This took place 12-15 November and was arranged primarily to enable all European countries to draw on one another's experience in the organisation and use of applied research.

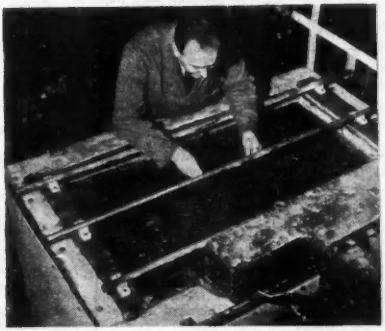
His Majesty's Government attaches great importance to contact with research activities in other countries. In addition to Scientific Attachés in Washington and Paris, it has now appointed an officer of DSIR, Mr. R. G. Silversides, M.Sc., as H.M. Scientific Attaché to Scandinavia.

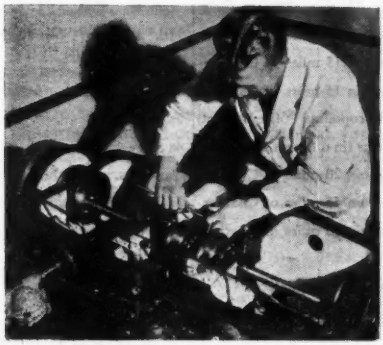
The Technical Information and Documents Unit, which formerly was attached to the Board of Trade, was transferred early in 1951 to DSIR, and now forms part of the Intelligence Division. Its main function is to make known and make available unpublished and semi-published scientific or technical documents, and to maintain records which will assist in the location of items by subject or by author. The Unit is also responsible for the selection of reports contributed by H.M. Government to the OEEC Documents Exchange Scheme and acts as the U.K. National Centre for the reception and distribution of reports from other member countries.

As part of a plan to make the activities of DSIR better known to commerce and industry, a number of firms in the Southern Region have been visited by an officer of Intelligence Division to find out how much use is being made of scientific information. Talks have been given to Chambers of Commerce and Regional Boards for Industry. This work will be extended. The regional activities of the Department were extended last year to Wales when the Industrial Association of Wales and Monmouth appointed a Scientific Liaison Officer, on loan from DSIR for a year, in order that close contact with the Department might be maintained.

Tin Research Institute

A notable event in May was the official opening by the Duke of Gloucester of the Tin Research Institute's new laboratories at Greenford, Middlesex. Much new equipment was installed during the year, and a notable achievement was the invention of three processes for tin alloy deposition





Above: Tin-nickel alloy plating being carried out on an industrial scale. Left: Setting-up an Underwood bearing - testing machine

Labour & The Chemical Industry

AN increase of 2,000 over the previous month and 17,000 more than at the end of 1950 was shown for the number of persons employed in the chemical and allied trades in Great Britain at the end of October, 1951, according to the analysis of civil employment in the *Ministry of Labour Gazette* (Vol. 59, No. 12).

Changes in the level of employment in the industrial analysis relate to employees only and exclude employers and persons working on their own account. The total numbers in Great Britain employed in chemicals and allied trades (in thousands) were 495.9 in October, compared with 494.4 in September, 479.0 at the end of 1950.

Unemployed persons (all classes) registered in the United Kingdom on 12 November, 1951, according to the industrial analysis showed 4,269 (2,421 men and 1,848 women) in the chemical and allied trades.

Placing work of the employment exchanges during the four weeks ended 24 October, 1951, showed that the following vacancies were filled in the chemical and allied trades:—Total 4,282; men (18 and over) 2,562; boys (under 18) 180; women (over 18) 1,210; girls (under 18) 330.

The total number of persons enrolled on the Technical and Scientific Register at 12 November, 1951, was 5,189. This figure included 3,796 registrants who were already in work but desired a change of employment, and 1,393 who were unemployed. During the four-week period 16 October to 12 November, the number of vacancies notified was 466. Vacancies filled were 217 and 295 were cancelled or withdrawn.

Only three stoppages of work through industrial disputes were reported in the chemical and allied trades in the U.K. during the first 11 months of 1951, and only 400 workers were involved.

Fatal industrial accidents in November, 1951, were fewer than in the previous month, the total of 122 comparing with 139 in October, and a revised figure of 155 for November, 1950. Only one death was recorded in the chemicals, oils, soaps, and allied industries.

National collective agreements or statutory orders provide for differential time rates of wages of manual workers according to locality. The chemical and allied trades according to a revised table in the *Ministry of Labour Gazette* were shown in the following table:—

Industry	Number of grades of localities	Description of highest grade	Difference between highest-rated grade and the lowest-rated grade in the time rates of adult male workers
Chemical and Allied Trades—			
Heavy Chemicals Manufacture (Association of Chemicals and Allied Employers)	2	London (within 15 miles of Charing Cross)	1d. an hour (productive and road haulage workers)
	2	London (within 12 miles of Charing Cross), Bexley Heath, Crayford, Dartford, Enfield, Erith, Hayes, Romford, Thames Ditton and Waltham	1½d. an hour (skilled engineers, electricians, pipefitters, boilermakers and coppersmiths)
Fertiliser Manufacture	3	London (within 15 miles of Charing Cross)	1½d. an hour (productive workers)
Plastics Manufacture (Chemical side)	2	London (within 15 miles of Charing Cross)	1d. an hour
Drug and Fine Chemical Manufacture	2	London (within 15 miles of Charing Cross)	4s. a week
Paint, Varnish and Lacquer Manufacture	2	London (Metropolitan Police District)	5s. a week
Soap, Candle and Edible Fat Manufacture	2	Grade A firms (in different localities)	4s. a week
Printing Ink and Roller Manufacture	2	London (within 20 miles of Charing Cross)	8s. to 10s. a week (according to occupation)
Match Manufacture	2	London (within 15 miles of Charing Cross)	½d. an hour
Glue and Gelatine Manufacture	2	London (within 15 miles of Charing Cross)	1d. an hour
Seed Crushing Compound Food and Provender Manufacture:			
Productive workers (England and Wales only)	4	London and 30 specified places	6s. a week
Electricians	3	Class A district (London—within 12 miles of Charing Cross)	10s. a week

Organic Reagents in Inorganic Analysis

A Short Review of Recent Developments

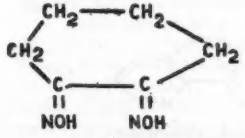
by WILLIAM I. STEPHEN, B.Sc., A.R.I.C.

THE rôle of organic reagents in general inorganic analysis has assumed great importance. Only a very few analytical processes are now conducted without their aid at some stage or other in the operation. When it is considered that even an ordinary acid-base titration cannot be conveniently effected without the use of an organic dyestuff, this fact becomes more obvious.

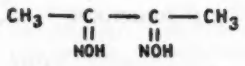
Many organic materials have the property of forming complexes with inorganic ions and thus can provide the means for their qualitative or quantitative analysis. To distinguish these compounds from normal organic substances, they have been named organic reagents. It is apparent that many of these compounds may be used in several distinct analytical processes. For example, dimethylglyoxime forms an exceptionallv stable, insoluble complex with nickel, a fact which has been used in the detection, and in the gravimetric and colorimetric estimation of this element. However, the nickel-dimethylglyoxime complex has also been used as an indicator in the argentimetric titration of cyanide where the appearance of the characteristic red precipitate denotes the end-point. Only in the first three cases can dimethylglyoxime be classed as an organic reagent; it is an integral part of the actual detection or determination under investigation. In general, organic substances are classified for use in analysis either as reagents, defined above, or purely as 'pointers' or indicators which denote the attainment of a certain stage in a chemical process. Several organic materials perform both functions but it is the purpose of this article to discuss only the recent and more important substances recommended for the detection or determination of various metals. The subject of new indicators has already been adequately discussed in a recent report published in THE CHEMICAL AGE.[1]

There is no need in an article such as this to detail the theories which have been advanced to account for the behaviour of organic reagents, nor is there any need to discuss the vast array of experimental evidence supporting these theories, although, in this latter respect the work of Fritz Feigl is of fundamental importance. Indeed, the first paper in English on the theory and uses of organic reagents in analytical chemistry was written by this eminent analytical chemist in 1936. Organic reagents had, of course, been known and employed for some considerable time before this, but it is to Feigl that all credit is due for the introduction of the theoretical concepts and the rationalisation of the subject into an exact science. To-day, organic reagents provide the analyst with a most powerful tool.

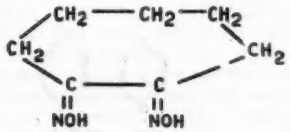
The 1 : 2-dioximes, the best known of which is dimethylglyoxime or, systematically named, diacetyl dioxime, possess the property of forming specific stable complexes with nickel. Dimethylglyoxime, in spite of its extensive applications, has certain disadvantages; it is insoluble in water and hence leads to contamination by precipitation with the nickel complex. Errors thus arise in gravimetric determinations since overwashing of the nickel precipitate can cause dissolution of the nickel complex into the filtrate. In an investigation of water-soluble 1 : 2-dioximes, Voter and Banks[2] have examined the most promising of these, namely, diaminoglyoxime, α-furildioxime, 1 : 2-cyclopentanedionedioxime, 1 : 2-cyclohexanedionedioxime and 1 : 2-cycloheptanedionedioxime. Only the last two are sufficiently soluble in cold water to allow their being used at room temperature.



NIOXIME



DIMETHYLGLYOXIME



HEPTOXIME

In accordance with modern convention, these substances have been named 'nioxime' and 'heptoxime' respectively.

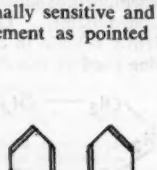
Nioxime forms a reddish-scarlet precipitate with nickel which provides an extremely sensitive test. The reagent is almost 20 times more soluble than dimethylglyoxime and can be used to precipitate nickel quantitatively down to a *p*H of almost 3. In spite of this, it is not possible to use the reagent in a single precipitation of nickel in the presence of iron. Heptoxime, on the other hand, combines all the advantages without the disadvantages. It precipitates nickel quantitatively from acid solution (*p*H 2.7 or greater) as a yellow insoluble complex. Nickel can be determined in the presence of tartrate, citrate, acetate, thiocyanate, sulphosalicylate and perchlorate anions and this provides a means of determining nickel in the presence of many other metals which normally interfere with its determination. Nickel can be rapidly estimated in steels containing both copper and cobalt.

For the determination of palladium, nioxime provides a more suitable reagent[3] since precipitation can be effected even in 0.1N acid (*p*H 1). The sensitivity is greatly increased and the precipitate can be digested, enabling filtration to be accomplished on hot solutions—a fact which results in a considerable saving of time over the lengthy dimethylglyoxime procedure.

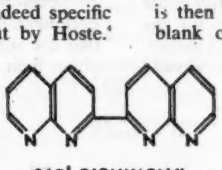
A recently developed copper-specific reagent is the substance 2: 2′-diquinolyl. Breckenridge, Lewis and Quick in 1939 showed that this substance formed an intensely purple-coloured complex with cuprous ions. These workers were investigating the properties of compounds containing the —N—C—C—N— chain, which form red-coloured complexes with ferrous iron: 2: 2′-dipyridyl and 1: 10′-phenanthroline are typical of this group.

2: 2′-Diquinolyl, however, does not complex with Fe^{++} but its reaction with Cu^{+} is exceptionally sensitive and indeed specific for this element as pointed out by Hoste.[4] The intense purple complex is stable over long periods of time, is readily extractable with an immiscible solvent such as *iso*amyl alcohol and does not require accurate control of *p*H for its formation. While several reagents have been recommended for the colorimetric determination of copper, *e.g.*, diethyldithiocarbamate and dithizone, none is entirely satisfactory. But before the use of a new reagent is justified, it must respond to certain conditions such as already described for the diquinolyl-copper complex. In view of this, the reagent appears admirably suited for the colorimetric determination of copper, since extraction of the Cu^{+}-specific complex with, say, *iso*amyl alcohol circumvents the need for prior separation even when coloured ions are present. 'Cuproine' as this reagent is termed has been thoroughly investigated by Hoste.[4,5] Since copper can readily be reduced to its monovalent state with hydroxylamine, the reagent has been applied more especially to the determination of copper in trace amounts, in biological materials[6]; less than 0.5 μg. copper can readily be determined. Indeed, as little as 0.02 μg. copper per ml. of tap water can be measured by this means.

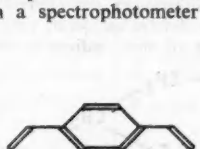
The available methods for the colorimetric estimation of beryllium using quinalizarin or aluminon are not altogether satisfactory, on account of certain undesirable properties of these reagents. Two natural dyes, alkannin and naphthazarin have been recommended for this element. The reaction of these dyes with beryllium was first noticed by Dubsky (1936) who recommended them for the qualitative detection of the element. The investigations of Underwood and Neuman[7] have shown that a suitable colour difference can be developed at *p*H 6.5 (approximately). The red colours of the dyes change to blue in the presence of beryllium. The *p*H of the sample is adjusted using a borate-mannitol buffer and the reagent added. The colour develops immediately and the sample is then compared with a similarly prepared blank on a spectrophotometer at 600 mμ.



2:2′-DIPYRIDYL



2:2′-DIQUINOLYL



1:10′- PHENANTHROLINE

The method is suitable only for small amounts of beryllium (1-20 μg.).

For the gravimetric determination of beryllium, α-picoline has been suggested.[8] With this reagent, beryllium can be quantitatively separated from manganese, cobalt, nickel, zinc and the alkaline earths. The reagent is added to the boiling test solution containing ammonium chloride and methyl orange, until the latter changes to yellow. Heating is continued on a boiling water bath for a few minutes and the solution filtered. The precipitated beryllium hydroxide is washed with dilute ammonium nitrate solution containing the reagent, dried and ignited at 1,000°C. The beryllium is weighed as BeO. When large amounts of zinc, manganese, cobalt and nickel are present, a double precipitation is generally required.

Antimony has been determined by Popov[9] with the dyestuff, methyl violet. After digestion of the antimony-containing sample with sodium dichromate and sulphuric acid, the digest is treated with hydrochloric acid and a slight excess of stannous chloride. Sodium nitrite is then added to the filtrate until the solution becomes a clear yellow, any excess nitrite being destroyed by shaking the acid solution. The antimony is precipitated by addition of methyl violet in hydrochloric acid and after vigorous shaking, the liquid is filtered. After washing with reagent solution the precipitate is treated first with 50 per cent sulphuric acid and then 30 per cent hydrogen peroxide, and again with sulphuric acid. Finally, the colour of the solution is measured absorptiometrically.

Antimony Spot Test

West and Conrad[10] have developed a new spot test for antimony using the substance, gossypol. As little as 0.5 μg. antimony can be detected in one drop of test solution (0.4-0.7N to HCl) by the following procedure. Place one drop of the solution containing antimony on a spot plate and add one drop of 20 per cent phosphoric acid. Mix well and add four drops of gossypol reagent (0.1 per cent in acetone). An orange or red precipitate indicates antimony.

A recent colorimetric method for determining bismuth has been recommended by Jean.[11] As reagents he uses rubeanic and silicotungstic acids. When bismuth is present in 0.1N nitric acid, these two reagents give a white turbidity. On heating, this disappears and the solution becomes brown, the colour being proportional to the amount of bismuth present. The reaction is sensitive to 20 μg. bismuth. Common metals which do not interfere with the determination are aluminium, magnesium, iron, chromium, alkalis and alkaline earths.

A new qualitative test for bismuth[12] consists of adding 1-2 drops of methyl red to the weakly acid test solution. On adding dropwise aqueous 0.1N chloramine T solution, the red test solution becomes colourless and then assumes a violet to lilac colour. The metals present with bismuth in elementary qualitative analysis, namely lead, copper, cadmium and mercury do not interfere. The test appears to have advantages over the colour reactions of thiourea and cinchonine.

Reagents for Cadmium

Several new reagents have been recommended for cadmium. Popov[13] uses methyl violet as precipitant but converts the cadmium finally to sulphide. The determination is completed by comparison of the CdS colour with standards obtained by adding aqueous ammonia and ammonium sulphide to the sesquioxide precipitate. The method appears suitable for determining the approximate content of cadmium ores.

Cadmium is normally determined gravimetrically as the 8-hydroxyquinolate (orinate). The determination may be completed titrimetrically by dissolving the precipitate in acid, adding excess standard bromate solution and determining the excess iodometrically. In this connection, a new direct volumetric procedure has been proposed by Belcher, Nutten and Stephen.[14] Using the organic substance, 3 : 3′-dimethylnaphthidine, they titrate cadmium in neutral solution with standard ferrocyanide. At the end-point, the red oxidised form of the diamine becomes colourless, the titrated solution assuming a pale green.

The problem of separating cadmium from copper in qualitative analysis without employing cyanide solutions has been investigated by several workers. A recent and apparently satisfactory method makes use of potassium xanthate,[15] C_2H_5OCSSK. This substance has been extensively employed as an organic reagent. The separation is achieved by treating the ammoniacal solution of copper and cadmium with acetic acid until it is just acid, and then adding

slight excess of potassium xanthate solution. Copper forms a dark-brown cupric salt which rapidly changes to the yellow cuprous form; cadmium forms a white precipitate. The solution is filtered, washed well with water and digested with 2N sulphuric acid. This dissolves the cadmium salt only, and after filtration and neutralisation with aqueous ammonia, cadmium can be detected by precipitation with hydrogen sulphide.

Magnesium Colour Test

Shashkin[16] has recently recommended a new colour test for magnesium. The sodium salt of 1-amino-2-naphthol-6-sulphonic acid gives a yellow precipitate with magnesium up to a dilution of 1 : 40,000. Most of the common ions do not interfere although the presence of iron will cause the magnesium precipitate to be marked by the formation of yellow ferric hydroxide. Copper and manganese do interfere. It is doubtful if this reagent possesses any distinct advantanges over the Magneson or Titan Yellow reagents, as the reaction undoubtedly proceeds via the formation of a coloured 'lake' It is apparently not as sensitive as the other two reagents.

Cystine,[17] a degradation product of certain proteins, has recently been used as a precipitant for copper, cobalt, nickel and zinc. When a 1 per cent solution of cystine is added to solutions of these metals in N hydrochloric acid and the solution made ammoniacal, complex precipitates are obtained. In these the metal atom is linked by the normal co-ordinate bonding to the organic molecule. Only the zinc compound, with the formula $(C_6H_{10}O_4N_2S_2)Zn$, is anhydrous; the others possess one molecule of water of crystallisation. Cobalt, nickel and zinc may be separated from calcium, barium and magnesium with this reagent. However, attempts to separate zinc from iron and aluminium in the presence of tartrate or sulphosalicylic acid are not wholly satisfactory, even when excess reagent is used.

The recent advances in the chemistry of the radioactive elements have called for accurate methods for the determination of thorium and uranium. Quite recently, Erämetsä has employed quinaldic acid as a reagent for thorium, since it precipitates this element quantitatively from cold solution. Under the same conditions, the rare earths are not precipitated, thus providing a means of extracting thorium from natural sources. Aluminium, beryllium and uranium interfere. Ryan *et al.*[14] recommend a 0.2 per cent aqueous solution of ferron to precipitate thorium, in the presence of tungsten, lanthanum, cerium, titanium, nickel and cobalt. The thorium is precipitated at a *p*H of 2-3.5 and the determination completed by ignition to ThO_2 at 900°C.

For the detection of uranium several organic materials have been proposed but none is entirely satisfactory. Oxine is perhaps the only suitable gravimetric precipitant but it is by no means the ideal reagent.

The colorimetric determination of uranium is best effected using chromotropic acid or aluminon, since these reagents show the greatest sensitivity. Lately, a new reagent for the gravimetric determination of uranium has been employed by Hovorka *et al.*[19] The reagent—isatin-β-oxime—forms a complex with uranyl salts which can be filtered, washed and ignited. The uranium is finally weighed as U_3O_8, accurate results being obtained over the range 1-240 mg. uranium.

For the qualitative detection of uranium, two Indian workers, Dasgupta and Gupta[20] use oxalohydroxamic acid. This substance gives an orange complex with the uranyl ion which is effective both for the detection and colorimetric determination of uranium. The limit of identification is 0.2 μg. at a concentration limit of 1 : 240,000.

Zirconium Investigations

Zirconium has been the subject of several recent investigations. Erämetsä[21] has developed the specific reagent, sodium flavianate for the detection and separation of zirconium. The reagent gives a yellow amorphous precipitate with zirconium—the only metal of the alkaline ammonium sulphide group with which it reacts. Lead, silver, mercury and thallium give precipitates, but these are readily removed from solution.

Another reagent, stated by Kumins[22] to be specific for zirconium, is mandelic acid. The precipitate obtained from 2N acid solution is filtered and ignited to ZrO_2. Hahn[23] has further investigated this reagent. Oesper and Klingenberg[24] have employed halogen-substituted mandelic acids since their use provides larger volumes of precipitate per unit weight of zirconium present. Phthalic acid appears to act selectively towards zirconium. Using this substance, Purushottam and Raghava Rao[25] precipitated zirconium

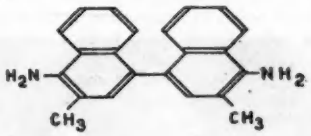
quantitatively from 0.35N hydrochloric acid. Zirconium can thus be separated by a single precipitation from most cations including the cerium earths, although when titanium, vanadium and chromium are present, a re-precipitation is necessary after dissolving the precipitate in 6N hydrochloric acid.

The work of Ryan and co-workers[26,27] on the estimation of the noble metals, palladium, platinum and rhodium, deserves special mention. Palladic palladium has the property of forming the most stable bonds in co-ordination compounds and its yellow complexes with 2: 2′-dipyridyl and 1: 10′-phenanthroline provide suitable means for its determination. The precipitate with 1: 10′-phenanthroline is the more insoluble although this reagent also precipitates platinum and iridium from concentrated solutions when those metals are present as the platini- or iridichlorides. Other reagents recommended for individual platinum metals are phenyl urea, thiophenol and thiobarbituric acid for palladium, *sym-di-o*-tolylurea for platinum and thiobarbituric acid for rhodium; all are described by Currah *et al.*[28]. In a later publication, Ryan[29] determines rhodium colorimetrically by forming an amber-to-red complex with 2-mercapto-4: 5-dimethylthiazole. Platinum and gold do not interfere and palladium may be eliminated by precipitation with dimethylglyoxime. Correction for the interference of iridium is made knowing the approximate concentration of this ion.

Use in Tungsten Determination

Organic reagents have found wide application in the determination of tungsten. One of the main problems in this connection is the development of a reagent to precipitate small amounts of tungsten directly and quantitatively in the presence of molybdenum without precipitating or co-precipitating this element. Not one of the many reagents proposed completely conforms to this exacting test. One of the more recent—4-amino-1-(4-aminophenyl)naphthalene[30]—precipitates tungsten quantitatively from normal hydrochloric acid. Under the conditions described, molybdenum does not interfere although ferric iron oxidises the reagent. Yoe's reagent[31]—*anti*-1: 5-di-(*p*-methoxyphenyl)-5-hydroxyamino-3-oximido-1-pentene gives an extremely insoluble complex with tungsten even in 0.5N acid, but co-precipitation of molybdenum occurs to some extent at this acidity. Without doubt, the most important reagent for small amounts of tungsten is toluene-2: 3-dithiol which is used for the colorimetric determination of this element because of the blue-green complex compound formed with the reagent. Unfortunately, the interference of molybdenum is serious but methods have been devised to overcome this. However, any further mention of tungsten here would only duplicate the contents of a comprehensive review recently published in THE CHEMICAL AGE.[32]

The use of the substance 3: 3′-dimethylnaphthidine has already been mentioned. In view of its exceptional sensitivity towards oxidants it has been recommended as a reagent for vanadium[33] and as a spot test for zinc.[34] As little as 0.1 μg. vanadate can be detected at a concentration limit of 1: 5 × 10⁵. The bright purple-red oxidation colour which is stable over long periods of time is admirably suited for the colorimetric determination of this element. Other oxidising ions must be absent.



3:3′- DIMETHYLNAPHTHIDINE

When applied as a spot test for zinc in the presence of the ferricyanide ion, a purple-red precipitate is formed. The limit of identification is 0.1 μg. at a dilution of 1: 5 × 10⁵.

Finally, two organic substances with promising uses as sulphide precipitants are thioformamide, $H.CSNH_2$, and thioacetamide, CH_3CSNH_2. Thioacetamide has been recommended in a series of papers by Flaschka and Jacobljevich[35] for the determination of tin, antimony, bismuth, molybdenum, copper, arsenic (III- and V-valent), cadmium and lead. The reagent is far superior to hydrogen sulphide as regards ease of application and in providing more granular sulphide precipitates which considerably facilitates filtration and subsequent washing. The determination is completed by weighing the metal as sulphide; with copper, after ignition to the oxide and solution in dilute acid, the determination is finished iodometrically.

Gagliardi and Loidl[86] employ thioformamide as precipitant. At the time of writing, they have used it to estimate copper and arsenic both alone and in presence of each other, in a similar manner to that used with thioacetamide. The general use of hydrogen sulphide is both time-consuming and messy. Both these reagents are readily obtainable, rapid in action and provide more suitable precipitates for routine quantitative analysis. Their ease of application in many determinations is a further distinct advantage.

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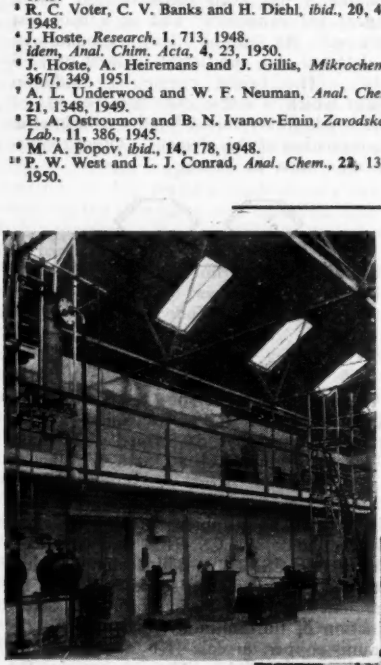
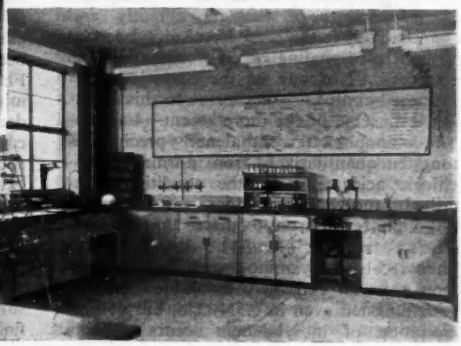


Laporte Laboratory

Below: The barium laboratory, part of Laporte Chemicals' new laboratory section opened on 8 May, 1951



Above: Pilot plant testing room

The Expansion of Oil Refining in Britain

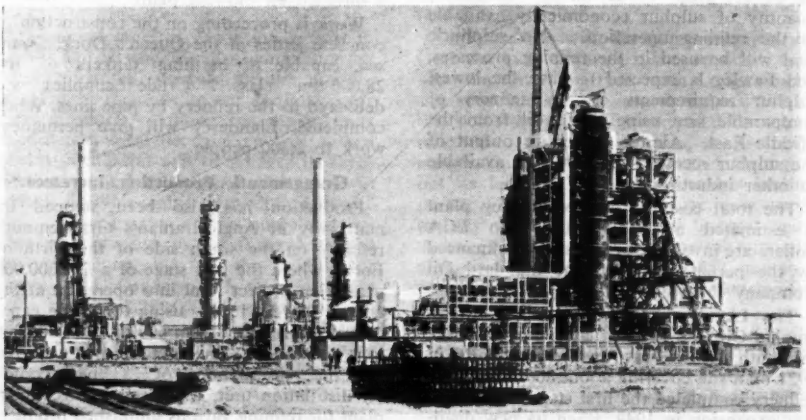
DURING the four-year period 1947-1950 inclusive, the annual quantity of oil refined in Britain increased by nearly 400 per cent, the respective figures for 1947 and 1950 being 2,470,000 and 9,284,000 long tons. In 1950 the total petroleum imports of the United Kingdom reached the record quantity of over 5,000,000,000 Imperial gallons, which represented an increase of almost 10 per cent over the previous year. Total imports of crude oil in 1950 amounted to 2,377,307,000 gallons, of which 1,951,444,000 gallons came from the Middle East, importations from other sources thus being approximately 18 per cent.

With the exception of lubricants, which showed an increase of about 66 per cent, the import of most refined products has decreased. Hitherto, the major emphasis in the programme of refinery expansion has been on fuels, but the production of lubricants can be expected to make rapid progress during the coming years, as projected plants are completed and come into operation and as the technique of manufacturing lubricants from Middle East crudes is developed.

During the first 10 months of 1951 approximately 13,000,000 tons of crude oil were imported into the U.K. which represented an increase of 75 per cent over the corresponding period of 1950. It was anticipated that by the end of 1951 importations would be at a level of about 15,000,000 tons annually. On 1 July, 1951, there were 17 plants in the United Kingdom with a combined crude capacity of 472,900 barrels daily and cracking capacity of 62,000 barrels daily. Britain's crude capacity was exceeded only by the United States, the U.S.S.R., the Netherlands West Indies, and Iran.

The post-war programme of refinery expansion was inspired primarily by the need to save large amounts of foreign exchange by refining crude oil instead of importing refined products mainly from dollar sources. Representing a capital investment of £125 millions, it aims at a refined petroleum production of more than 20,000,000 tons a year in 1933. Due to the need to refine as much as feasible to offset the loss of Abadan, U.K. refineries had reached the level of 20,000,000 tons a year by October, 1951. Additional refining capacity now under construction will raise the U.K.'s annual total to 26,000,000 tons in 1953.

The most notable event which took place last year was the opening of the new Fawley



A general view of the main refinery units of the new Esso plant at Fawley, opened by Mr. Attlee during September

Refinery of the Esso Petroleum Co., Ltd., which is the largest single refinery in the United Kingdom and Europe at the present time. Work on the new plant was started in July, 1949, and completed four months ahead of schedule, the refinery being opened by Mr. Attlee—then Prime Minister—in September, 1951. American technicians and foremen planned the refinery and supervised the construction, but the labour employed was nearly all local and many leading British firms worked as sub-contractors. Nearly two-thirds of the equipment was built in Britain.

Fawley's 41,000-barrel-per-day fluid catalytic cracking unit is capable of producing 1,000,000 gallons of high octane motor spirit per day. All important petroleum products, excluding aviation petrol but including turbo jet fuel and lubricants, will be produced when the refinery is fully completed in 1953. Including the capacity of the old refinery, Fawley will have a maximum capacity of 6,500,000 tons per annum when in full operation in 1953. It will then employ over 2,500 men.

Sulphur Recovery Plant in 1953

In addition to the refining units a sulphur recovery plant is scheduled for completion in 1953 and is planned to produce about 12,000 tons of 95.5 per cent chemically pure rock sulphur a year by a controlled oxidation process. The plant has been designed to extract from crude oil the maximum quantity of sulphur economically available in the refining operation. No sulphuric acid will be used in the refining processes, and Fawley is expected to have the lowest sulphur requirements of any refinery of comparable size using crude oil from the Middle East. Almost the entire output of the sulphur recovery plant will be available to other industries.

The total cost of the new Fawley plant is estimated at £37,500,000. No ECA dollars are involved, since Fawley is financed by the parent company—the Standard Oil Company (New Jersey).

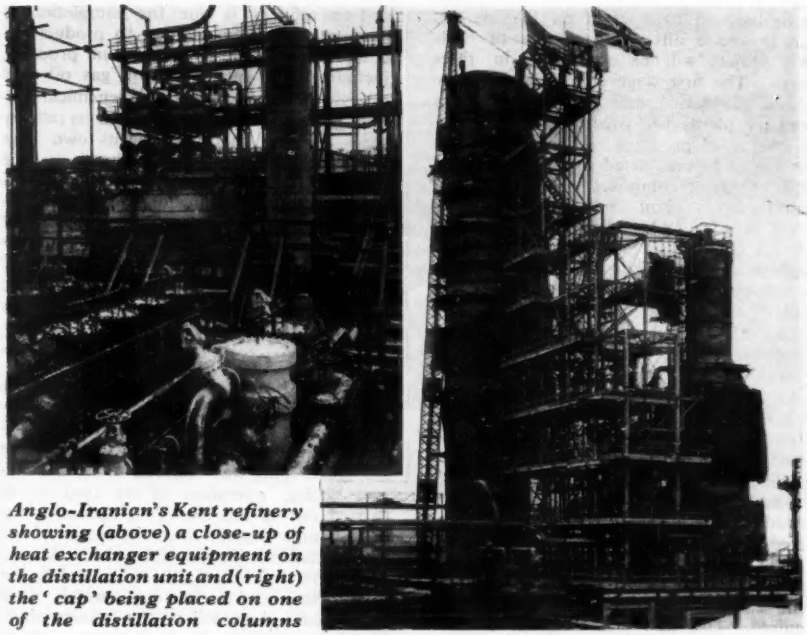
The Llandarcy Refinery of the Anglo-Iranian Oil Co., Ltd., situated near Swansea in South Wales, was opened originally in 1921 on a site covering about 800 acres. This refinery completed the first stage of its post-war expansion in 1949, when its new distillation unit came into operation several months ahead of the original target date. This was the first major refinery unit to be constructed in Britain after the war. The interim stage of the expansion programme provided essentially for the installation of a 45,000-barrel-per-day crude oil unit and stabiliser plant, with a minimum of treatment plants and off-site facilities. In conjunction with the older refining plant, these extensions brought the total capacity at Llandarcy to 3,000,000 tons per annum. It was envisaged that the capacity of 3,000,000 tons a year would later be reduced to the planned level of 2,500,000 tons when some obsolete units had been taken out of service. By the middle of August, 1951, however, annual capacity had been increased to 4,000,000 tons by re-vamping some thermal units and converting them into topping units.

The expansion programme also provides for a 10,000-barrel catalytic cracking unit and a new lubricating oil plant, both of which are due for completion in 1952. The latter includes a 3,500-barrel-per-day propane deasphalting unit, a 1,250-barrel-per-day furfural solvent-extraction unit, a 1,700-barrel-per-day M.E.K. dewaxing and wax recrystallising plant, and a 350-barrel-per-day wax treatment and slabbing plant. In order to provide feed stocks for the lubricating oil plant and the catalytic cracker, the vacuum distillation capacity of the refinery will be increased by the installation of a 17,000-barrel vacuum unit. There will also be an SO_2 solvent extraction plant and a bitumen air blowing plant.

Work is proceeding on the construction of concrete jetties at the Queen's Dock, Swansea, capable of berthing tankers of the 28,000-ton class. Crude supplies are delivered to the refinery by pipe lines. When completed, Llandarcy will give permanent work to 2,500 people.

Grangemouth Production Increases

Production has also been stepped up materially at Anglo-Iranian's Grangemouth refinery on the south side of the Firth of Forth, where the first stage of a £20,000,000 expansion project went into operation at the end of March, 1951, raising the crude capacity of the refinery from 600,000 to 1,800,000 tons per annum. This increase was achieved by the installation of a new crude oil distillation unit, together with treatment plant for refining various unfinished products derived from the crude. The main tower of the crude oil unit, a 76-ton fractionating



Anglo-Iranian's Kent refinery showing (above) a close-up of heat exchanger equipment on the distillation unit and (right) the 'cap' being placed on one of the distillation columns

column manufactured in Britain, was delivered to the refinery and erected in January, 1950.

The second stage of expansion is now in progress and is scheduled for completion by mid-1952. It will provide for the production of premier grade motor spirit and for special products. Among the major units included is a catalytic cracking unit with a vacuum distillation unit to prepare its feedstock and a catalytic polymerisation plant to produce a stable spirit from its 'exhaust' gases. The capacity of the completed refinery was planned to be about 1,800,000 tons per annum, but by the middle of August, 1951, Grangemouth was producing at the rate of 2,250,000 tons a year, an increase of 25 per cent.

An unusual feature in the construction of the refinery is the use of 'buoyancy' type foundations. Since no solid foundations exist for some considerable depth, a hollow reinforced concrete raft, subdivided into compartments with tops and bottoms making a complete series of watertight cells, was designed to support the new heavy units of the refinery.

In connection with the refinery project at Grangemouth, a new tanker terminal has been built at Finnart on Loch Long, which can accommodate the largest tankers. From this point the crude is transported by a 60-mile 12-in.-diameter pipeline to Grangemouth, this pipeline being buried throughout its length. The existing tanker berths in the Grangemouth docks are now used entirely for the shipment of finished products. Work on the new crude oil terminal at Loch Long began in May, 1950, and the first tanker to off-load at Finnart arrived in February, 1951.

Another notable undertaking is Anglo-Iranian's Kent Refinery (Isle of Grain), for which official approval was finally given in June, 1950. This will be a full-scale refinery with an annual capacity of about 4,000,000 tons and is intended to supply markets in the southern counties. It has

been designed to operate on Persian and Kuwait crude oils or a mixture of both. This project will be completed in three stages. The first stage comprises an atmospheric distillation unit with the necessary auxiliary plants for sweetening and blending the chief products. These extensions are due to be completed in the first half of 1952. Stage 2 comprises a lubricating oil manufacturing plant and should be completed early in 1953. The third stage is also due for completion in 1953 and includes a catalytic cracking plant for converting the heavier types of semi-refined oils into high-grade motor spirits. Plants for the manufacture of other products requiring special processes may be installed at a later date, constituting a fourth stage.

An output of 2,000,000 tons annually will be achieved when the initial operations are started in June, 1952. The capacity will be raised to 3,000,000 tons in December, 1952, and finally to 4,000,000 tons by June, 1953. Altogether about 1,500 persons will be employed when all three stages have been completed.

Due to the scarcity of fresh water, seawater will be used for cooling purposes, and some 2,500,000 gallons per hour will be required. Two new jetties will be built to accommodate tankers up to 32,000 tons deadweight.

When the Kent Oil Refinery is in full operation in 1953, AIOC's U.K. refining capacity will reach the figure of 10,430,000 tons a year.

At their Pumpherston refinery the company process 180,000 tons per annum, consisting mainly of shale oil.

Shell's Post-War Programme

Satisfactory progress has been made with the £30 million post-war refinery programme which Shell has undertaken in the United Kingdom. The new Stanlow refinery started operations in November, 1949, over a month in advance of schedule. Since then, the first distillation unit has been operating at its full capacity of 1,000,000 tons per annum. The second distillation plant came on stream in June, 1951, trebling the refinery's capacity to over 3,000,000 tons of crude oil annually. Output has since been increased to 3,800,000 tons. A sulphur recovery plant from which 10,000 tons of sulphur can be obtained annually has also been installed.

This refinery is due for completion in January, 1952. In addition to producing a comprehensive range of petroleum products, including high quality petrol, gas oil, fuel oil, synthetic detergents and chemical solvents, it will also make full use of its refinery gases as raw materials for its own large chemicals-from-petroleum industry. The completed plant will include a catalytic cracking and reforming unit, a polymerisation plant, and units for final treatment of the products. The new cooling tower for the refinery is the world's largest concrete structure of its kind, rising to over 340 ft. and having a capacity of 5 million gallons of water an hour.

Construction Feat

A welded steel absorber column (weight 240 tons, length 170 ft., diameter approximately 10 ft.) was raised to vertical at Stanlow by huge gantries specially designed for the task. This was believed to be the biggest lifting operation of its kind to be carried out in the United Kingdom. On the 225-mile journey from the works of the manufacturers, Messrs. Babcock & Wilcox, at Renfrew, Scotland, the unit had to be transported in three sections, which were assembled and welded on the refinery site.

Initial operation of the post-war extensions at Shell Haven started in November, 1950, when the first distillation plant was commissioned to produce a designed intake of 6,000 tons/stream day of crude oil, bringing the crude oil capacity of the refinery to its planned level of 2¾ million tons per annum. A doctor treating plant provides facilities for the treatment of approximately 1,300 tons a day of straight-run gasoline from the distilling unit. A thermal reforming plant was completed and put on stream some months ahead of schedule in April, 1951. It is designed to process about 1,200 tons/stream day of light gasoline. A preparation plant for the production of bitumen feedstock will have a capacity of 2,500 tons/stream day and is scheduled for completion during 1952. Shell Haven will then produce a complete range of finished products. It now refines 3 million tons a year.

For transporting crude oil to Stanlow and Shell Haven from the Middle East, 28,000-ton tankers will be extensively used. To accommodate tankers of this size, the Manchester Ship Canal Company are constructing an oil dock at Eastham. From this

A general impression of the complexity of the pipeline systems in the crude oil distillation area at Llandarcy refinery

point the crude oil will be piped a distance of five miles to the Stanlow refinery.

In comparison with the developments at Stanlow and Shell Haven, there has been little expansion at the Heysham refinery. This refinery was built by the Government during the war and closed down in July, 1946. Shell purchased the refinery plant early in 1948 and operations were started shortly afterwards. In addition to the three original crude oil distillation units, the plant now includes a thermal reforming unit and a viscosity breaking unit. The present capacity of this refinery is 1,500,000 tons per annum.

Work is proceeding on the development of the Coryton Refinery of the Vacuum Oil Company, the total cost of which is expected to exceed £10,000,000. This refinery is intended primarily for the production of lubricating oils, and will have a planned capacity of 850,000 tons a year. Its most notable feature will be a catalytic cracking unit.

The British Government has approved in principle a refinery which the Caltex/Trinidad Leaseholds Group plans to erect between Southampton and Portsmouth, on the eastern shore of Southampton Water. According to an announcement in 1949, the refinery will have an annual crude capacity of approximately 1,000,000 tons.

At Ellesmere Port, Lobitos Oilfields, Ltd., refine 100,000 tons of crude per annum. A Stratford hot lube oil treating plant of 220-barrels-per-day treating capacity was installed during 1950.

Manchester Oil Refineries specialise in the production of lubricating and transforming oils, white oils, liquid paraffin, and other high grade mineral oils and chemicals. The present capacity of their Trafford Park Refinery is 175,000 tons per annum, but this will be substantially increased by developments due for completion early in 1952.

Alterations being carried out by Berry Wiggins & Co., Ltd., at Kingsnorth provide for a new Foster Wheeler two-stage distillation unit of 2,000-barrels-per-day capacity. The present annual capacity of this refinery is 100,000 tons.

Supplies of crude were, of course, affected by the unilateral actions and intransigent attitude of the Persian Government, which led to the disappearance—perhaps only temporary—of this source of oil. In 1950, about 25 per cent of Britain's crude oil imports came from Persia. Since the total production of the Middle East now approaches 100,000,000 tons per year and is still being expanded, Persian oil is not likely to be of critical importance to the long-term requirements of British refineries.

Fertilisers in 1951

by D. P. HOPKINS, B.Sc., F.R.I.C.

ATTEMPTING to survey the year of 1950 for fertilisers, the writer (CHEMICAL AGE, 1951, **64**, pp. 73-75) laid emphatic stress upon the re-entrance of the economic factor as a dominant trading influence. It is now only too starkly clear that 1950 was no more than a 'shape of things to come'. The final removal of subsidies from fertilisers took place on 1 July, 1951. Shortly before that, the new grassland fertiliser subsidy scheme had also been withdrawn, a piece of politico-economic infanticide that strangely provoked few questions and no discussion.

Exceptional Price Rises

The second dose of de-subsidisation was much less palatable than the first. No doubt the original plan was to shave away the subsidies in two more or less equated instalments but between 1 July, 1950, and 1 July, 1951, many items of cost in fertiliser production and distribution had moved sharply upwards. The intended 'second half' inevitably became the old half plus all the new cost rises. For phosphatic fertilisers the price rise was exceptionally severe and probably for the first time in the history of the industry the cost of a unit (1 per cent) of sol. P_2O_5 was almost exactly the cost of a unit of ammoniacal N, a new economic relationship that in no way reflected the quantitative ratio in which these two major plant-foods should be used in most systems of farming.

As in 1950 there was considerable 'stock-piling' of fertilisers in the two months preceding the date of de-subsidisation. Manufacturers were exceptionally busy in May and June. It can only be said that they became exceptionally un-busy after 1 July. No more difficult trading period than the second half of 1951 has been experienced by the industry since the depression of the early 'thirties.

It has long been one of the industry's severest problems that its products are required in two sharp seasons—autumn and spring—together covering some 4 to 4½ months of the year. Steady all-the-year-round production requires an abundance of storage. Hitherto this problem had been overcome—neither easily nor fully but at any rate with a sufficient degree of practical effectiveness—by storing to the limit in works themselves, then later in merchants' stores, and finally in farm barns.

The first victim of 'real prices for fertilisers' was this system of diverse storage. Works soon found that production must largely flow into their own storage space and by October most factories found themselves in dire need of extra space or outward orders. Far from being prepared to order fertilisers in advance, few farmers were prepared even to give indications of their probable spring requirements. By the end of the autumn the position of the industry was acutely difficult. Some indication of this—and of its extent—is given by the fact that the officially imported cargoes of superphosphate, required to balance the estimated shortages of acid-rationed home industry, could often not be taken in. In other words, the sulphur shortage proved to be a smaller contracting influence than the effect of the new prices upon consumer demand.

Subsidy Reintroduced

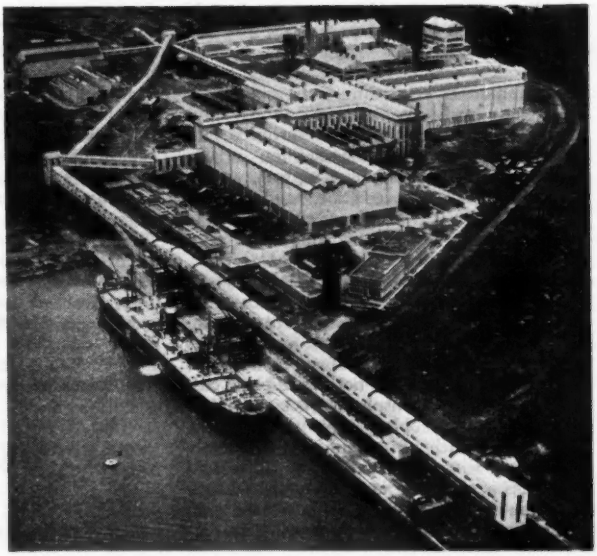
The General Election did not help. Farmers seemed inclined to adopt a 'wait-and-see' attitude, believing that a new government might bring back fertiliser subsidies. There was little expectation of this in the industry; on the whole it was believed that any new economic relief farmers might obtain would be in the form of increased crop prices through a further farm price review. As is now well known, the new Minister of Agriculture and Fisheries reintroduced a 30 per cent subsidy for phosphatic fertilisers on 29 November, with retrospective application to 1 July. It is still too early to assess the consequences of this sudden reversal in policy but at least 1951 came to an end with a noticeable lifting of depression from the fertiliser industry, whose immediate problem now will be to compensate for the lost output and lost intake of materials of the July-November period. Works which were able to take in all the phosphatic raw materials offered to them in that period, or which were able to

store their full production, are entering 1952 in a strong position. Not all the phosphatic material now in store will long defer the production-curtailing effect of sulphuric acid shortage.

Is the return of a subsidy for phosphates sufficient to offset the loss of subsidies paid on mineral forms of all three main nutrients? It is a reasonable assumption that it will be sufficient. *Pro rata* the rise in price of nitrogen was not severe; and although the rise in price per ton of potash was fairly steep, potash fertilisers are highly concentrated (50 to 60 per cent) and therefore the relative rise in cost per acre is not great. The new subsidy will ease the farmer's fertiliser costs where they hurt him the most—on phosphates. If, however, an abnormal demand for phosphates occurs (on the superficial argument that this plant-food is subsidised and the others are not) every one will have to start thinking again. When the sulphur crisis broke in 1950, the immediate possibilities of expanding phosphate production and use in this country came to an end. So far the reality of this harsh blow has been obscured by the artificial supply/demand developments of partial and complete de-subsidisation. Those who imagine that the new subsidy for phosphates takes the situation tidily back to 1949 will soon find that the 1949 production situation no longer exists. Farmers may have to learn that the subsidy-carrying fertiliser is the one they cannot readily obtain.

What progress has been made during 1951 towards liberating phosphatic fertilisers from their acute dependence upon sulphur? There are two roads of relief—to develop methods of producing acid from pyrites, anhydrite, and like materials, and to develop new fertiliser processes that do not require sulphuric acid (or as much of it) to break up the rock phosphate complex. The British superphosphate industry has played its full part in creating a new company that is to produce a large tonnage of acid from native anhydrite; another commendable development has been the mission of sulphur exploration in South America, undertaken by one of Britain's best-known fertiliser manufacturers, and of this the early reports have been highly encouraging. However, there cannot be immediate relief from these long-term operations.

Throughout the year technical interest has been turned to alternative methods of



Aerial view of Fisons' latest factory at Immingham, which was opened in April, 1951. The works cover some 45 acres

making phosphatic fertilisers. The use of nitric acid as a replacement for sulphuric acid has (at any rate in public) received more attention than the thermal or fusion processes. A major difficulty in nitric acid processes is the production of calcium nitrate, a moisture-absorbing substance that is so poor a replacement for the conditioning calcium sulphate in superphosphate made with sulphuric acid.

The Dutch Process

A notable paper by Dr. Plusjè, of the Netherland State Mines, where the nitric acid method is already in large-scale use, was read in London in February (THE CHEMICAL AGE, **64**, 309). In the Dutch process the calcium nitrate is removed by cooling and crystallisation, the phosphate-acid solution having an excess of nitric acid; the remaining excess is then neutralised with ammonia, the final solution, with or without potash salts addition, being concentrated and granulated. A 20-20 N-P_2O_5 fertiliser is produced if potash salts are not added at the pre-granulation stage. A wider survey of European processes that use nitric acid has appeared in America (Clark and Hardesty). In this country, after some years of research, I.C.I. have announced the small-scale production of a 'nitrophosphate' fertiliser with 12.7-12.7 analysis for N and available P_2O_5 respectively. In this process excess nitric acid is not used, rather less than the theoretically calculated amount being in fact mixed with phosphate rock; the calcium nitrate produced is not removed but is converted into ammonium nitrate by the addition of ammonia and ammonium sulphate. The material thus produced can be dried and granulated. It was given extensive field tests last year and a larger plant, still of pilot size, is being built.

One of the considerations that has to be faced in developing nitric acid processes is that nitrogen-phosphate and not straight phosphate fertilisers are produced. It has long been a great merit of superphosphate that it can be used at not too high a cost for dressing the phosphate-deficient field, a common soil problem in British farming. Moreover, much of the nitrogen inevitably associated with phosphate in the nitric acid products is of the nitrate kind, quickly available and quickly washed out of the soil. Phosphate dressings on poor soils are required just before or at sowing time, which is not also the best time for applying high dressings of nitrate-nitrogen. For this reason the thermal treatment of phosphate rock, which gives a straight phosphatic fertiliser, deserves as much, if not more, investigation. Also, thermal methods are longer established than nitric acid processes, the German Rhenania process having been first introduced during World War I.

Fuel and power problems are no doubt formidable obstacles to the development of fusion methods in Britain to-day. In the Chemical Research Laboratory's Report published during the year some attention (in addition to investigations of nitric acid methods) was given to thermal treatments of phosphate rock. Serpentine was chosen as the silica-containing agent; the two main conditions found in laboratory experiments were (a) a SiO_2/P_2O_5 ratio greater than 2, and (b) rapid quenching of the fusion product. Both these conditions are essential if a high proportion of the phosphate is to be made citric-soluble. Fusion temperatures are between 1,400° and 1,600°; a suitable third component that would reduce this temperature has yet to be found. However, there is a hint in recent Japanese research that a potassic mineral can be used for this purpose. (Nagai, 1950.)

Overseas Developments

If at home the industry has been preoccupied with price problems and the impacts of acid scarcity, there have been one or two notable developments abroad. In Germany a forceful recognition of the rôle of magnesium has been made, new potash fertilisers with added and declared contents of magnesium now being produced; these are mixtures of potash and magnesium sulphate. Manufacturers and soil scientists in Eastern Germany believe that many of the troubles previously blamed upon soil acidity have in fact been caused by magnesium shortages. In Australia and New Zealand, and especially in the latter country, the application of fertilisers from aeroplanes has been making excellent progress (Lynch).

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Trends in Analytical Procedure

by J. R. MAJER, M.Sc., Ph.D., A.R.I.C., D.I.C.

THERE has been a tendency, maintained and even enlarged during the last twelve months, for analysis to become a matter of physical technique or biological method rather than chemical procedure. The ready availability of radioactive isotopes such as C_{13} has encouraged estimations of substances, for example, penicillin G by the isotope dilution method, or identification of them upon a paper chromatogram. The technique of paper chromatography itself has been widely adapted and developed for separating such widely different mixtures as organic acids and inorganic metal salts. Microbiological assay is a branch of analysis which is acquiring more and more importance as fresh antibiotics come into use or fresh substances of biological significance are isolated. The most recent applications of this method have been to the estimation of vitamin B_{12}, the anti-pernicious anaemia factor, and the adrenocorticotropic hormone. Another technique which is rapidly becoming established is flame photometry, and this has already been successfully adapted for the routine estimation of sodium and potassium.

Colorimetric Comparison

Where a chemical method is involved and an element or radicle is determined by a quantitative reaction it has become usual to employ a reagent which will produce a colour. The colour is then matched against a standard sample in a colorimeter or spectrophotometer. Often the precipitation of an insoluble complex is prevented by the addition to the solution of a colloid such as gelatin or gum arabic. This method has the great advantage of simplicity and brevity over the older methods of gravimetric analysis, and it is with the latest developments in the former method that this article will largely deal. The problems of this type of analysis are to find a reagent which will react with the substance or ion to form a coloured product. The reagent should be specific, or if this is not possible, a procedure must be devised to isolate the substance or remove the interfering congeners. There should be a quantitative reaction with the substance in question and the complex product should be stable at least within the limits of error over the time required for a complete estimation. When the reaction is complete the coloured product should not settle from solution and any tendency to do this should be prevented by the use of a suspending agent, usually a colloid which will kept the solution homogeneous. Finally the solution should obey Beer's Law over the range of concentrations which it is desired to cover.

Fluorescent Analysis

The use of filters can often increase the accuracy of a determination and in some cases it is preferable to work in the ultra-violet region of the spectrum. An alternative procedure which can be used in some cases involves the formation of a product which, though not coloured, is fluorescent under ultra-violet light. The light emitted can be compared with that emitted from a standard sample and the concentration deduced. As the fluorescence of many organic substances can be detected at very low concentrations this can provide a very sensitive method of detecting traces.

As a further refinement of the method the metal complexes may be removed from the aqueous phase by extraction with an organic solvent, and this can give greater accuracy by removing interfering ions or reducing the bulk of solution. The table given overleaf lists some of the organic substances which have been used in the colorimetric or spectrophotometric determination of metallic ions in solution.

8-Hydroxy Quinoline.—During the year there have been many references to the use of 8-hydroxy quinoline for the detection and determination of a variety of metal ions. At the present time it must be the most versatile reagent in the analytical laboratory and has been recommended for such diverse ions as scandium and lithium. The reagent itself and its halogen derivatives can be estimated by taking advantage of the intense green colour which they produce with the ferric ion. When this is dissolved in 2-methoxyethanol, small quantities may be determined spectrophotometrically. This is of value clinically, since the iodo derivatives of

Element or ion	Reagent or ion	Range or accuracy	Reference
Cobalt	Tetraphenylarsonium thiocyanate	—	A.C. Nov., 1680
Zinc	Dithizone	2 to 13 mμg.	A.C. Nov., 1699
Zinc	Dithizone	0 to 5 μg.	A. April, 220
Nickel	Perchloric acid	0.05 per cent	A.C. April, 580
Nickel	1, 2-Cyclohexanedione dioxime	—	A.C. March, 448
Nickel	Furil dioxime	—	A.C., March, 500
Nickel	*β-iso*Thioureidopropionic acid	0.005 mg.	A.C. July, 1014
Nickel	1,2-Cycloheptanedione dioxime	—	A.C. October, 1486
Gold	*p*-Dimethylaminobenzal rhodanine	0.2 μg.	A.C., April, 653
Tellurium	Iodotellurite	0.2 to 2 p.p.m.	A.C. April, 651
Molybdenum	Phenylhydrazine hydrochloride	2 to 10 p.p.m.	A.C. February, 304
Molybdate	Catechol	50 μg.	A.C. January, 188
Magnesium	Thiazole yellow	0.8 per cent	A.C. May, 751
Magnesium	8-Hydrox Yquinoline	7.5 per cent	A.C. May, 754
Tungsten	Stannous chloride, potassium thiocyanate	—	A.C. May, 781
Cerium	Cerium IV	0.025 μg.	A.C. March, 453
Lithium	8-Hydroxy quinoline	—	A.C., March, 478
Rhenium	Thiocyanate	0.1 to 2.5 mg.	A.C. March, 497
Manganese	Permanganate	0.1 per cent	A.C. March, 506
Germanium	Oxidised haematoxylin	0.08 to 1.6 p.p.m.	A.C. July, 1023
Vanadium	Peroxyvanadic acid	0 to 125 p.p.m.	A.C., June, 901
Palladium	2-Mercapto-4,5-dimethyl thiazole	—	A. May, 310
Copper	Sodium dithiocarbamate	—	A. May, 317
Iron	Triphenylmethyl arsonium thiocyanate	1 to 10 μg.	A. September, 548
Calcium	Picrolonic acid	10 to 100 μg.	A. August, 482
Titanium	8-Hydroxy quinoline	—	A. August, 485

A.C.—*Analytical Chemistry*. A.—*The Analyst*.

8-hydroxy quinoline such as 5,7-diiodo and 5-chloro-7-iodo-8-hydroxy quinoline are used as drugs in the treatment of amebiasis and it is frequently desired to measure small quantities in the urine.

The analysis of rocks for their lithium content has been simplified by a new fluorometric procedure. The previous gravimetric method was slow and the separation of other alkali metals was often incomplete. The basis of the latest method is the complex formed between lithium and 8-hydroxy quinoline and is specific. The complex fluoresces in alkaline alcohol and this may be measured upon a photoelectric fluorimeter. Separation from the original ore is carried out by the distillation procedure and sodium and potassium are removed by the use of alcohol and ether. The method can also be applied to the preparation of standard lithium solutions from reagent quality salts. Magnesium in solutions extracted from plant leaf tissue has been estimated by conversion to the 8-hydroxy quinoline complex, but the method has not the accuracy of the alternative technique employing Thiazole Yellow. Scandium may be estimated gravimetrically using 8-hydroxy quinoline as the precipitant. All other ions forming precipitates with the reagent must be removed first and as little as a hundred thousandth of a mol of scandium can be measured. The precipitate formed has the formula $Sc(C_9H_6NO)_3C_9H_7NO$.

Another reagent which has widened its scope of usefulness is sodium diethyldithiocarbamate. This has been used for the determination of copper for some time, but it has been shown that it can also be used for bismuth, cobalt, chromium, iron, nickel and uranium. The complexes formed can be extracted from their water solution with chloroform over a wide range of acidity, and by controlling the acidity, copper can be separated from uranium and chromium. As all the elements mentioned will interfere in the estimation of copper it is important that they should be removed.

Complexes of metals with 8-hydroxy quinoline can be titrated with potassium permanganate but the method is not particularly accurate. The substitution of 8-hydroxy quinaldine which is oxidised to methyl quinolinic acid by the permanganate gives a more quantitative reaction and has been used to provide a volumetric method for magnesium.

The Alkali Metals.—The estimation of potassium by sodium cobaltinitrile is facilitated by a new method of storing the reagent, which is very unstable in aqueous solution. As it is quite stable in the solid form the reagent is precipitated from a freshly made aqueous solution with 99 per cent alcohol, and the precipitate suspended in alcohol after decantation. The container is shaken directly before use and as soon as the sodium cobaltinitrite comes into contact with the aqueous potassium solution it dissolves. The reagent may be stored for months and does not have to be kept in the dark and protected from temperature changes.

The determination of potassium in potash salts and fertilisers can be carried out by measuring the radioactivity of the sample.

No pre-treatment other than grinding is required, and the method is suitable for control where there are no other radioactive mineral substances likely to interfere.

Potassium and sodium have been determined using the technique of flame photometry in a variety of solutions and minerals. Two new methods for the determination of sodium have been described. The first, devised for the estimation of sodium in serum, uses a magnesium uranyl acetate reagent containing 80 per cent of alcohol. This produces a simultaneous precipitation of the sodium and the protein. This is removed by centrifuging and the amount of sodium calculated by the diminution in strength of the reagent. The method is only approximate but a determination can be carried out in 15 minutes.

The second method has been developed to estimate the amount of sodium in samples of aluminium and its alloys. A sample of the metal is distilled *in vacuo* at a temperature of 900°C. and the sodium, which distils over, is determined in the usual way using zinc uranyl acetate. The accuracy of the method is limited by the size of sample which can be treated, and as little as 0.0001 per cent has been determined.

The Alkaline Earth Metals.—A modification of the well-known method for the estimation of calcium with picrolonic acid has been devised in order to measure the amounts of calcium in small samples of sea water. As little as 1 μg. in 2 ml. of sea water can be measured colorimetrically. The method depends upon the loss in intensity of a solution when the calcium salt is precipitated.

Strontium in Sea Water

The concentration of strontium in sea water has been determined by an entirely different method. A sample of radioactive strontium salt is added to the sample of sea water and the fraction of the total strontium that is co-precipitated with barium sulphate on addition of barium chloride measured by the loss in activity of the solution. By the use of flame spectrophotometry it is possible to estimate the amount of strontium that must be added to the solution in order to bring back the strontium emission to the value before precipitation.

High purity vanadium is often produced by fusing the pentoxide with calcium metal in a vessel lined with refractory magnesia. It has therefore become of interest to estimate the amounts of calcium and magnesium which occur as impurities in vanadium metal. In a recent method the large excess of vanadium was removed by converting it to the complex with cupferron and extracting with chloroform. The calcium and magnesium remaining in the aqueous phase were then estimated as calcium oxalate and magnesium ammonium phosphate.

Magnesium in Plants

The concentration of magnesium in plant tissue has been measured by taking advantage of the colour produced by the magnesium ion on treatment with Thiazole Yellow. The complex is stabilised under alkaline conditions with polyvinyl alcohol, and interfering ions are eliminated or compensated for by the addition of hydroxylamine, copper, aluminium, calcium, manganese and phosphate. The method is more sensitive than previous colorimetric procedures, and is more rapid than the volumetric or gravimetric methods available. The amount of magnesium in samples of cast iron has been measured by dissolving the sample in hydrochloric acid, extracting the iron with *iso*-propyl ether, removing manganese by electrolysis with a sodium amalgam cathode, forming complex ions with citric acid of any remaining interfering ions, and carrying out a double precipitation of the magnesium as phosphate. Zirconium ions interfere with this method.

Zinc and Mercury.—The separation of zinc oxide from zinc powder, in which it is always present as an impurity, has been achieved by the use of ammonium acetate, which dissolves the oxide and leaves the metal, thus providing a method of determining the amount of oxide present. When zinc is present in small quantities in copper it can be estimated by an extraction procedure using the reagent dithizone. As dithizone is a very non-selective reagent, use is made of the preferential rate of extraction of the dithizone complexes from the aqueous phase with chloroform. The addition of zinc to a solution containing the ferricyanide and ferrocyanide ions leads to the removal of ferrocyanide ions from the solution as insoluble zinc ferrocyanide. Belcher and others have shown that the solution will then oxidise certain organic compounds which are oxidised by ferricyanide alone.

Among those mentioned are naphthidine and dimethyl naphthidine.

The residues of sprays upon the peel of apples contain mercury in some cases, and a method has been devised for checking that the quantities are sufficiently low. After the tissues have been freeze dried, the organic matter is digested with a sulphuric/nitric acid mixture and the mercury determined spectrophotometrically as the dithizone complex. The mercuric ion and acetone have been observed to combine to give a complex organomercury compound with the production of a hydrogen ion. This provides a method of determining the mercuric ion by titration with standard alkali. Acid radicles such as bromide, chloride, iodide or thiocyanate can then be determined with silver nitrate in the conventional manner.

Titration of Mannitol Complex

Germanium.—An aqueous solution of germanium dioxide reacts with mannitol to form a strong complex acid, and this phenomenon can be made use of to estimate germanium. The mannito-germanic acid is strong enough to be titrated directly with sodium hydroxide solution, using phenolphthalein as indicator. This volumetric procedure is preceded by the precipitation of the germanium as sulphide. Quinquevalent arsenic interferes with the estimation by its buffering effect upon the solution. To obviate this when determining germanium in the presence of arsenic, the solution is reduced with sulphur dioxide until the arsenic is all reduced to the innocuous tervalent form. Excess of the sulphur dioxide is removed by boiling the solution.

Solutions of quadrivalent germanium give an orange-to-pink colour when treated in acid solution with phenyl fluorone. This substance, prepared from benzaldehyde and triacetyl-hydroxy-hydroquinone is 2,3,7-trihydroxy-9-phenyl-6-fluorone. The precipitation of the germanium complex is prevented by the use of gum arabic, and the coloured solution so obtained can be compared with a standard absorptiometrically. The germanium can be separated from interfering substances by distilling it with hydrochloric acid and the method is sensitive enough to make it suitable for the examination of small samples of coal, coke and flue dust.

When solutions of germanium are treated with oxidised haematoxylin a purple colour is developed. The precipitation of the complex is prevented by the addition of gelatine and the germanium can then be determined colorimetrically.

Selenium and Tellurium.—The amount of selenium in organoselenium compounds has been measured by digesting a weighed sample with sulphuric acid followed by nitric acid. When all traces of organic matter have disappeared the solution is cooled and diluted. Urea is added to remove any traces of nitrogen oxides and a measured volume is mixed with excess potassium iodide solution, when iodine is liberated equivalent to the selenium. The iodine is then titrated with sodium thiosulphate in the normal way, using starch as indicator.

A new method of determining the amounts of selenium and tellurium in copper has been described by F.D.L. Noakes. After solution of the sample in nitric acid and removal of the nitrous fumes, the selenium and tellurium are precipitated by reduction with stannous chloride in hydrochloric acid. The precipitate is redissolved in bromine/hydrobromic acid mixture and is either reprecipitated and the elements estimated gravimetrically, or alternatively, a volumetric method can be used which involves separation of the two elements with sulphur dioxide.

Iodotellurite Ion Determination

Small amounts of tellurium have usually been determined by producing colloidal tellurium and measuring it photometrically. Particle size variation and deviations from Beer's Law have made this method unreliable and it has been suggested that the iodotellurite ion, which is soluble and highly coloured, can be determined spectrophotometrically. Bismuth forms a coloured iodo complex and must be removed, ferric and cupric ions oxidise the acid iodide solution and therefore interfere by producing iodine. Selenite is reduced to colloidal selenium by the reagent.

The selenium and also the bismuth are removed at low concentrations of iodine and acid by extraction with an amyl alcohol/ethyl acetate mixture.

Fluorine.—The fluorine in organic compounds may be analysed by simple combustion at 900°C. in a quartz tube with a platinum catalyst. The products of combustion are collected and titrated with sodium hydroxide using phenolphthalein as

indicator. When only small quantities of fluorine compounds are present in air or water, this method is not satisfactory, and a method has been published for the determination of four physiologically active organic fluorine compounds under these conditions.

The substances were sodium fluoroacetate, methyl fluoroacetate,2-fluoroethanol and di-*iso*propyl fluorophosphonate. These compounds are removed from air by scrubbing with hexyl alcohol, which also serves as a high-boiling solvent in the conversion of the combined fluorine to fluoride with sodium. The fluorine in the sample is converted to sodium fluoride, which is removed from the hexyl alcohol by washing with water. The concentration of sodium fluoride in this aqueous layer can be determined either volumetrically or colorimetrically. In the volumetric procedure the sodium fluoride solution is acidified and buffered with chloracetic acid/sodium hydroxide buffer and titrated with standard thorium nitrate solution using sodium alizarin sulphonate as indicator.

If the fluorine compound is present in water instead of air then an alternative sequence of operations must be carried out. The organic fluorine is converted into inorganic fluoride by heating the water solution with a mixture of silver perchlorate, perchloric acid and potassium metaperiodate. When the mixture is distilled in the presence of glass wool the fluorine appears in the distillate as silicon tetrafluoride. Once again the inorganic fluoride is estimated by titration in a buffer solution with standard thorium nitrate using Solochrome Brilliant Blue BS as indicator.

New Fluorine Procedure

An entirely different procedure has been devised by R Belcher and J. C. Tatlow for the estimation of fluorine in organic compounds. In this case the fluorine is converted into inorganic fluoride by heating it with sodium in a specially designed nickel bomb. The fluoride is then estimated gravimetrically as lead chlorofluoride. J. C. Cropper has also been publishing work upon this problem and has described a method in which, after a preliminary decomposition of the fluorine to fluoride, the fluoride is determined potentiometrically by the addition of lead nitrate solution, in the presence of excess sodium chloride and a mixture of ferrous and ferric chloride. Lead chlorofluoride is precipitated, and at the end-point the ferrifluoride ion dissociates, giving a sharp change in the 'redox' potential.

Solid halocarbons containing fluorine may be decomposed at 1,100°C. in a current of moist oxygen, and the fluorine determined colorimetrically using the ferric iron/salicylic acid reagent. The accuracy is less than half that of the previous method.

Dioxime Reagents

Iron, Cobalt and Nickel.—The dioximes of *cyclo*hexanedione (nioxime) and *cyclo*heptanedione (heptoxime) have been investigated as reagents for the determination of nickel in calcium when there is more than a trace of iron present. They behave similarly to dimethylgloxime, and in alkaline solution, in the presence of an oxidising agent, produce unstable reddish brown colours which have a similar absorption spectrum. When, however, the red inner complex of nickel with 1,2-*cyclo*hexanedione dioxime is stabilised with gum arabic, it is insensitive to changes in *p*H, absorbs strongly at 550 mμ and conforms to Beer's Law. This has been made the basis of a spectrophotometric method for measuring the quantity of nickel in calcium metal.

Furil dioxime has also been used as a reagent in the colorimetric determination of nickel. The complex may be extracted from aqueous solution with 1,2-dichlorobenzene and this makes it possible to remove the nickel from solutions which contain coloured interfering ions such as iron or chromium.

The measurement of the purity of nickel of high grade has been simplified by a differential spectrophotometric method using the green colour of the nickel ion in perchloric acid solution. It is said to be extremely accurate.

At the other end of the scale trace amounts of nickel can be determined by the use of a new reagent, β-*iso*thioureidopropionic acid. In ammoniacal solution this acid reacts with nickel ions to give a highly coloured complex. It is supposed that this is produced by the breakdown of the acid to mercaptopropionic acid which then chelates with the nickel. With the reagent amounts of nickel down to a cencentration of 0.6 mg. in 100 ml. have been determined by the colorimetric method.

The Vogel reaction for the detection of

cobalt, which involves its reaction with thiocyanate ions in the presence of mixed organic solvents, has been studied and it has been decided that the characteristic blue colour is due to the formation of the $Co(CNS)_4$ ion. A note has also appeared claiming that 1-nitro-2-naphthol is not a suitable reagent for the precipitation of cobalt. Some writers have suggested that this reagent is superior to the conventional 1-nitroso-2-naphthol, but the nitro-naphthol prepared by the oxidation of nitroso-naphthol probably contains some of the starting material, and the precipitate obtained with such material is due to this impurity. When the nitro-naphthol is purified by steam distillation and crystallisation from alcohol it gives no precipitate with cobalt.

No Interference with Iron

Most of the substances suggested for the micro colorimetric determination of iron suffer from interference from nickel and cobalt. This can be obviated by the use of a new reagent, triphenylmethylarsonium thiocyanate, which gives an isolatable complex with iron of the formula $(Ph_3MeAs)_8.Fe(CNS)_6$. The complex is insoluble in water, but soluble in organic solvents such as chloroform, ethylene dichloride and *o*-dichlorobenzene. For the purposes of colorimetric estimation it is removed from the aqueous phase with one of the solvents.

Molybdenum.—A red colour is produced when solutions of molybdenum are treated with phenylhydrazine hydrochloride in 50 per cent acetic acid. The colour is stable and is preferable to the thiocyanate colour, as it does not have to be extracted into organic solvents. Iron interferes when present in comparable amounts, and must be removed by selective reduction. A red colour is also produced when molybdic acid is treated with catechol and this has been developed for the colorimetric determination of molybdate. The use of sodium bisulphite and an optimum amount of sodium hydroxide stabilises the complex. The measurement of small quantities of rhenium in the presence of a proponderance of molybdenum, can be carried out only if the molybdenum can be removed first. This has been achieved by forming the ethyl xanthate complex and extracting it from the aqueous phase with an organic solvent, preferably carbon tetrachloride/benzene mixture. The rhenium itself is estimated by converting it to the thiocyanate complex with sodium thiocyanate.

Titanium, Indium and Osmium.—Microgram quantities of indium in beryllium have been measured by a method involving the extraction of the indium from the solution containing beryllium, and any impurities that the beryllium compound may contain, with chloroform, after conversion to the 8-hydroxy-quinoline complex. After concentrating the extracts and decomposing the organic matter, the indium is separated from iron and molybdenum with diethyl ether. The indium concentration is determined polarographically by the definite step which it gives from a base electrolyte consisting of hydrochloric acid, sodium formate and hydrazine hydrochloride.

The amount of osmium present in an organic compound can be measured on the micro scale by a new technique due to F. P. Dwyer. This has hitherto been difficult owing to the ease of formation and volatility of osmium tetroxide. This has prevented the decomposition of organic matter by the digestion procedure with sulphuric and nitric acids. The osmium is converted to sodium osmate by fusion of the sample with sodium carbonate and sodium peroxide. The sodium osmate formed is treated with hydrobromic acid and converted into hydrogen hexabromosmate. The osmium is then measured colorimetrically using thiourea.

8-Hydroxy quinoline has also been used for a variety of separations and determinations during the year. K. Gardner has used it for the photometric determination of small amounts of titanium.

Hydrogen Peroxide Used

Hydrogen peroxide itself gives a colour reaction with titanium, but this method uses the colour produced when titanium solutions containing hydrogen peroxide are extracted with a solution of 8-hydroxy quinoline in chloroform. This procedure is more sensitive than with hydrogen peroxide alone, but is less selective, and zirconium and vanadium must be absent. The compound in the chloroform layer is said to be a peroxidised titanium 8-hydroxy quinolinate.

Chromium and Manganese.—The manganic ion forms a complex with acetyl acetone which has no oxidising action upon acidified potassium iodide. In the presence of acetyl acetone, manganese tetrachloride loses chlorine and forms the stabilised

trihalide. The chlorine which is thus evolved chlorinates the acetyl acetone present and this chlorination can be reversed in the presence of acidified potassium iodide with the consequent liberation of iodine. By titrating the iodine liberated with sodium thiosulphate it is possible to find the amount of tetrachloride present in a mixture of the trichloride and tetrachloride.

The analysis of manganese bronze has been facilitated by the observation that copper and lead may be separated from as much as 2 per cent of tin by electrolysis with a perchloric/nitric acid mixture as electrolyte. This obviates the time-consuming use of hydrogen sulphide. After the copper and lead have been removed the other constituents such as manganese, tin, iron and aluminium can be determined in the usual manner.

The proportion of chromium in samples of catgut has been measured by the use of diphenylcarbazide.

Estimation of Platinum Metals

The Platinum Metals.—A technique has been devised for the detection of platinum, palladium and rhodium in the presence of each other or their more common congeners. Ryan uses *p*-nitroso diphenylamine for this purpose, and the interference of strongly coloured ions is prevented in the detection of palladium, by removing the palladium complex from the coloured aqueous solution with an organic solvent. This procedure may be made the basis for a method of separating palladium quantitatively from the other platinum metals. When testing for platinum or rhodium, the interference of palladium is prevented by the addition to the solution of dimethyl glyoxime. If testing for platinum in the presence of rhodium the rhodium complex is removed by extraction with an organic solvent. On the other hand neither platinum, rhodium nor iridium interfere with the detection of palladium with *p*-nitroso diphenylamine. The test is carried out by adding an aqueous alcoholic solution of *p*-nitroso diphenylamine to a neutral or feebly acid solution of the platinum metal—the colours developed are orange or red. Using the drop scale technique, as little as 0.01 μg. can be detected on a filter paper.

Ryan has also suggested the use of 2-mercapto-4,5-dimethyl thiazole as a reagent for the determination of palladium. The other platinum metals interfere, but if the concentration of rhodium is kept below 10 μg. per ml. the interference is negligible. The interference of platinum is overcome by an extraction procedure, and this can be adapted to separate small quantities of palladium from solutions containing comparatively large amounts of platinum, rhodium or gold. Iridium solutions are almost completely decolorised and so palladium can be determined in the presence of large amounts of the iridium ion ($IrCl^{''}$).

The determination is carried out in acid solution in the presence of ethyl alcohol, and the amount of the palladium complex is determined colorimetrically. The maximum absorption of the complex is in the ultra-violet, but satisfactory results have been obtained using filters with maximum transmission at 430 mμ.

The extraction procedure for small amounts of palladium consists in forming the complex with *p*-nitroso diphenylamine, and extracting this from the aqueous solution containing the other platinum metals with ethyl acetate or chloroform. The extracts are run down and the organic matter destroyed with sulphuric and nitric acids before the palladium is determined as above.

R. S. Young on the other hand has suggested the use of dithizone in the determination of platinum, palladium and gold. His method is particularly applicable to the beads obtained in the assay of precious metals. The palladium can be extracted as the dimethylglyoxime complex with chloroform and as the dithizone complex with carbon tetrachloride.

Toxicity of Gold

Organic compounds containing gold have been used in medicine and the toxicity of some of these compounds made it necessary to be able to determine traces of gold in body tissues and fluids. A method has been published which can detect as little as 0.2 μg. of gold. After a preliminary ashing and digestion procedure to remove organic matter the gold solution is treated with a reagent containing *p*-dimethylaminobenzal rhodanine and the colour developed measured spectrophotometrically.

Iridium.—Iridium may be determined in the presence of lead by removing the lead as phosphate and estimating the iridium by hydrolytic precipitation, or the iridium may be determined directly in the presence of

lead by the use of 2-mercapto-benzthiazole. This gives an orange precipitate with solutions containing the iridium ion and this may be collected and reduced to the metal.

Zirconium.—Fumaric acid has been proposed as a reagent for the precipitation of zirconium. In sub-normal solutions of hydrochloric acid it is completely removed from solution as a gelatinous complex containing an atom of oxygen in addition to the zirconium fumarate radicle. When ignited, this complex gives the oxide. The reagent separates zirconium from aluminium, beryllium, uranium, nickel, barium, calcium, iron, manganese, thorium and the ceria earths with only a single precipitation, while a double precipitation removes vanadium, chromium, titanium and tin. *m*-Cresoxy acetic acid is also an extremely selective reagent for zirconium.

Vanadium.—The reagent originally suggested for the detection of small amounts of zinc has been adapted for use with vanadium. The substance, 3,3-dimethyl naphthidine, is 3,3-dimethyl-4,4-diamino-1,1-dinaphthyl, and is oxidised during the course of the test to a reddish-violet substance by the ferricyanide ion. Other ions such as Cr_2O_7, MnO_4 and VO_3, which have oxidising properties, can produce this colour, and Belcher has used this as a test for vanadium.

Organic Analysis

Carbonyl Compounds.—The presence of formaldehyde in mixtures containing large quantities of its polymerisation products has not been easy to detect or measure. In the presence of phenylhydrazine and potassium ferricyanide, a characteristic red colour is produced and although this is time-sensitive, it can be stabilised sufficiently to provide the basis for a quantitative estimation.

A similar procedure has been devised for the measurement of small quantities of a variety of carbonyl compounds. This makes use of the red colour which is developed when the 2,4-dinitrophenylhydrazones of carbonyl compounds are treated with a base. This colour does not vary a great deal with the structure of the individual carbonyl compound unless the molecule is markedly unsaturated and can thus be compared with a standard spectrophotometrically.

Substitutes containing a carbonyl group are particularly suitable for this type of analysis because of the ease with which they form coloured products, and the problem of the measurement of small amounts of benzil upon treated cloth has been solved by the reaction of the extracted benzil with *m*-diethylaminophenol. The dye produced is bluish-red in colour and has a red fluorescence, and the reaction can be used to estimate the phenol as well as the benzil.

Vanillin, on the other hand, has been assayed by a very simple procedure involving oxidation with alkaline hydrogen peroxide, and back titration of the alkali unreacted with the acids produced.

Hydroquinone.—The polymerisation of methacrylic acid is inhibited by the addition of small amounts of hydroquinone and it is therefore convenient to measure the relative proportions of the two substances in a sample. R. Belcher and W. I. Stephen have used the reducing action of hydroquinone to convert the ferric ion to the ferrous state in a solution of ferric ammonium sulphate. The amount of ferrous ion present is estimated absorptiometrically using *o*-phenanthroline, and the interference of the remaining ferric ion is prevented by converting to the ferrifluoride ion.

Pyridines.—While large numbers of dyes contain the pyridine nucleus, and many of these are formed by using the reactivity of methyl groups attached to the ring, a satisfactory colour reaction for the detection of the lower homologues has only just recently been described. The reagent proposed by E. F. G. Herrington is a mixture of a phenol, chloroform and sodium ethoxide. With this reagent it is possible to detect as little as 0.1 per cent of γ-picoline in β-picoline or 2,6-lutidine, and in the absence of these or other bases 0.0005 ml. of γ-picoline will produce a detectable colour. If the phenol is replaced by thiophenol, then much more brilliant colours are obtained, and this reagent is particularly suitable for the detection of single bases. The detection of β- and γ-picoline in 2,6-lutidine can also be carried out using a reagent containing dinitrochlorobenzene and acetamide.

Nitro-naphthalenes Sulphonated

2-Nitro-naphthalene can be estimated in the presence of 1-nitro-naphthalene, dinitronaphthalene or naphthalene itself by sulphonating the sample, reducing it with zinc dust, and measuring the intensity of the light emitted upon u.v. irradiation.

Some Recent I.C.I. Developments

EARLY in 1951 the United States announced that her exports of sulphur were to be radically reduced. During the last 25 years Britain has become almost entirely dependent on sulphur supplied from America, but the British chemical industry must now replace American sulphur, especially in its chief use, the manufacture of sulphuric acid. Alternative methods of making the acid have to be found, or where they already exist, developed. Iron pyrites can be used to replace sulphur, but this material has to be imported from Spain.

Imperial Chemical Industries, Limited, however, have for 20 years manufactured sulphuric acid at their Billingham Division, using anhydrite (anhydrous calcium sulphate) as the basic raw material. The anhydrite is mined beneath the site of the Billingham plant, which to-day uses one million tons of anhydrite yearly to produce 100,000 tons of sulphuric acid. The company has plans in hand to increase the production of this plant to 175,000 tons a year (1/10th of the requirements of British industry) at a cost of over £2,000,000. This will be done by additions to existing plant. Work has already commenced, and the new installations are expected to come into operation during 1954. The use of the anhydrite process can be extended, because deposits of this material are found in other parts of Northern England.

I.C.I. recently offered to place its technical knowledge of the anhydrite process at the disposal of some of the largest users of sulphuric acid, if they would join I.C.I. in financing a new anhydrite-sulphuric acid plant. The offer was accepted and the United Sulphuric Acid Corporation formed. A plant will be built at Widnes at a cost of £3,500,000 to produce 150,000 tons of acid yearly. This plant will not immediately improve the situation, because, even given the highest priority for materials, it may take three years to complete.

Other methods of reducing British consumption of sulphur are being employed. As a stop-gap measure, I.C.I. made arrangements, for itself and other companies, to import sulphuric acid from the Continent at a rate equal to approximately 2½ per cent of British production. The company recently announced that it had perfected a process for making nitrophosphate fertilisers to take the place of superphosphate fertilisers. The use of nitrophosphate fertilisers will effect a permanent economy, because every ton of superphosphate requires 4/10ths of a ton of sulphuric acid. The new fertilisers have undergone field trials this year, and a pilot plant for their manufacture has been erected at Billingham. One problem in making nitrophosphates that research has overcome is the removal of calcium nitrate which is formed by the basic reaction of nitric acid with phosphate rock. This chemical has a

The £2,000,000 'Ardil' plant at Dumfries

great avidity for moisture, and soon changes a solid fertiliser into a fluid mass.

The chemical industry is perfecting several new fibres. I.C.I.'s contributions in this field are 'Ardil' protein fibre and 'Terylene' polyester fibre. A £2,000,000 plant at Dumfries is already producing 'Ardil' fibre. The basic raw material is groundnut meal which contains about 50 per cent protein. This is dissolved out of the groundnut meal with dilute alkali and the solution is filtered off. This solution is then acidified and the soluble impurities filtered off. The solid protein obtained is dissolved in dilute caustic soda and is then extruded through spinnerets with very fine holes into an acid coagulating bath and—after special treatment with formaldehyde—is washed and dried.

Blended With Wool

Though 'Ardil' fibre is very similar to wool it is not intended to be used alone. With wool it will be made into worsteds, woollens, hosiery, blankets, felts, carpets and hats. These blends, containing up to 50 per cent of 'Ardil' fibre, are almost impossible to distinguish from all-wool fabrics. Perhaps the most important outlet for the fibre will be in mixtures with cotton or with viscose staple fibre. Added to these fibres, it improves handle and draping properties and makes them warmer, softer and less creasable. Unlike a natural fibre, the dimensions of the 'Ardil' fibre can be controlled.

'Ardil' fibre is a most useful complementary fibre costing much less than wool. It has the great advantage that its price will not fluctuate violently—a most important point.

'Terylene' polyester fibre is at present being made at a pilot plant in Lancashire, the material produced being used for development work by leading firms in the British textile industry. Plans are under way for a plant at Wilton, North Yorkshire, to produce 5,000 tons of 'Terylene' yarn a year. Plant and buildings are being designed and many of the main contractors have been selected. Manufacture of equipment is being started and construction work will begin early in 1952. The basic raw materials, terephthalic acid and ethylene glycol, will come from the nearby oil cracker.

'Terylene' polyester fibre is extremely versatile. Textiles may be made from it ranging from fine voiles, chiffons and lingerie fabrics, to heavy canvasses and wool-like blankets, and it can be made into fishing lines or ships' hawsers. It can be produced in either short staple or continuous filament forms. The staple fibre may be spun into yarn, according to type, in the cotton, woollen, worsted or flax systems, producing characteristically different yarns and fabrics. Fabrics made from 'Terylene' polyester filament yarn are smooth and silk-like in appearance and, owing to the high strength of the filaments, may be very fine.

Other products in I.C.I.'s many spheres of activity have attracted notice during 1951. The new I.C.(P). intravenous anaesthetic 'Anavenol' K, has aroused considerable interest among veterinary surgeons. This anaesthetic is particularly suitable for cattle and horses. Its use has permitted a number of births in valuable cattle to be effected by caesarian section, an operation previously rarely performed on these animals. 'Avlosulfon', another I.C.(P). product, has been of great assistance to doctors in the treatment of leprosy.

I.C.I. has designed electrolytic cells for producing elemental fluorine, and has supplied a number of these cells to research and industrial establishments. Fluorine first came into prominence because it was needed to make uranium hexafluoride. Among its peacetime uses is in the conventional oxy-acetylene torch. Extremely high temperatures are obtainable if the torch is supplied with hydrogen and chlorine trifluoride, instead of oxygen and acetylene.

Gross Flotation Method

A FLOTATION process that is not so well known as selective flotation was described to the American Institute of Chemical Engineers at its 44th annual meeting recently. Gross flotation, as it is called, can be used to effect an almost complete separation of all suspended solids, a property of great use in waste disposal. First used to recover pulp from white water in the paper industry, the gross flotation method is now being adapted in America to the recovery of many other suspended materials. In both flotation processes air bubbles are used to separate the solids, but whereas in selective flotation the foam is only stabilised enough to preserve the bubble and its adhering particles, in gross flotation a stiff froth of myriads of tiny bubbles results in the flotation of all the finely divided settleable and non-settleable particles from a suspension.

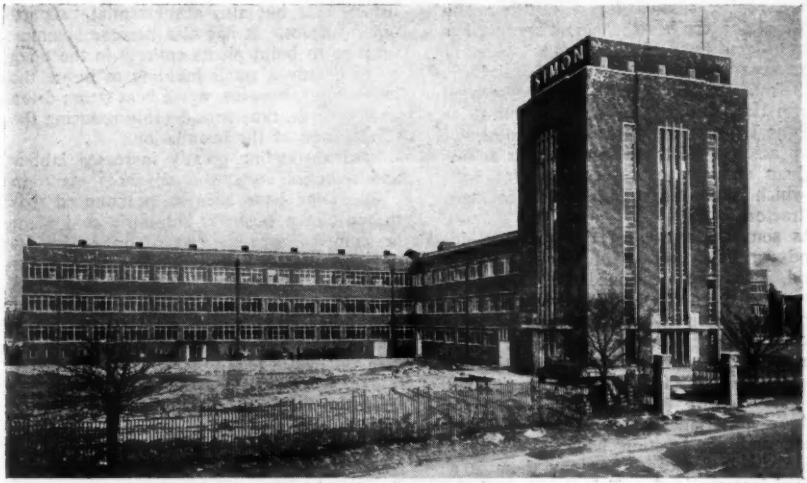
H_2SO_4 Plant Construction by Simon-Carves, Ltd.

BOTH during and after the second World War there has been intense activity in the building of sulphuric acid plants, not only in the United Kingdom but in many other countries. The persistence of the post-war demand for new plant construction has been remarkable and offers the strongest contrast to the slump that followed the first World War, when the expansion of acid production for military purposes left the market surfeited with acid supplies and acid-making equipment.

The boom of the last few years arises from a number of causes. There has, of course, been the normal replacement of obsolescent plant, but there has also been a large increase in the world demand for sulphuric acid, due partly to a general growth of industrialisation and largely to the great expansion of particular acid-using industries, notably rayon manufacture, oil refining, the production of chemicals from petroleum, and the manufacture of fertilisers. Moreover, at the time when the building of new sulphuric acid plants might otherwise have been expected to fall off, it received a new stimulus from the shortage of American sulphur; this has led to the placing of many contracts for new pyrites-burning plants and for the conversion of existing sulphur-burning plants to pyrites.

As far as Britain is concerned, there is the additional fact that even pyrites, being mainly imported, is not an assured source of sulphur supply; as is well known, large schemes are now on foot for the manufacture of sulphuric acid from our only indigenous raw material, anhydrite.

The situation thus briefly described is reflected in many of the contracts received by Simon-Carves, Ltd., in recent years. As instances, some half-dozen plants of various capacities (some of which are now in use) have been ordered by Courtaulds for rayon production in several factories, and a plant was completed some little time ago for a rayon concern in Egypt. Several plants have been built for the Shell organisation for sulphuric acid production at overseas oil refineries and for sulphur recovery and sulphuric acid concentration at their chemicals-from-petroleum plant at Stanlow; an



Part of the Simon Group research and development buildings at Cheadle Heath which were opened during July

A scale model of a 150-ton outdoor pyrites-burning acid plant with Nichols Freeman flash roasters. This model is based on a plant now under construction for a chemical and fertiliser concern in Athens

acid concentration plant was also recently commissioned for British Petroleum Chemicals at Grangemouth. Sulphuric acid plants for fertiliser production have been completed in Egypt, and Britain's largest single-unit plant with the exceptional capacity of 240 tons per day was commissioned not long ago at Fison's new superphosphate factory at Immingham; a large plant is at present being erected for a fertiliser and chemical concern in Athens, and another has been ordered from New Zealand.

As regards the production of sulphuric acid from anhydrite, it is of course well known that Imperial Chemical Industries and the United Sulphuric Acid Corporation are proceeding with very large plants at Billingham and Widnes respectively, for both of which Simon-Carves are acting as main contractors.

As some indication of the post-war demand for acid production throughout the world, it may be mentioned that since 1945 forty-three Simon-Carves Monsanto contact plants have been completed or put in hand in ten countries in four continents, the aggregate output of these plants amounting to approximately 3,500 tons of sulphuric acid per day.

Many important developments in plant design and construction have taken place within the last decade. Among them is a marked increase in the efficiency of catalytic conversion in contact plants by the adoption of multi-stage converters; two-stage conversion in separate converters was common before the war, whereas four-stage conversion is now widely used, with all the stages taking place in a single converter. Much progress has also been made in waste heat recovery, and large sulphur-burning acid plants nowadays not only supply all the steam required for sulphur-melting, blower drives, etc., but also a substantial 'exportable' surplus. It has also become common practice to build plants entirely in the open or with only a small building to house the instruments, blowers, waste heat steam drum and so forth, thus considerably reducing the capital cost of the installation.

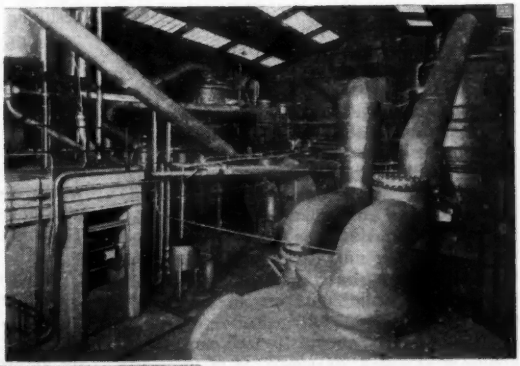
Notwithstanding greatly increased labour and material costs, the advances made in plant design have been so pronounced that the cost of a post-war sulphuric acid plant in comparison with that of an equivalent pre-war plant has risen far less than might have been expected.

A noteworthy development in connection with pyrites-burning plants is the introduction of the Nichols Freeman flash roaster with full waste heat recovery, a system that is now being incorporated in practically all new Simon-Carves 'metallurgical' contact plants. Nichols Freeman flash roaster equipment is also supplied by Huntington, Heberlein & Co., Ltd., who are now associated with Simon-Carves as a wholly-owned subsidiary company, and by their

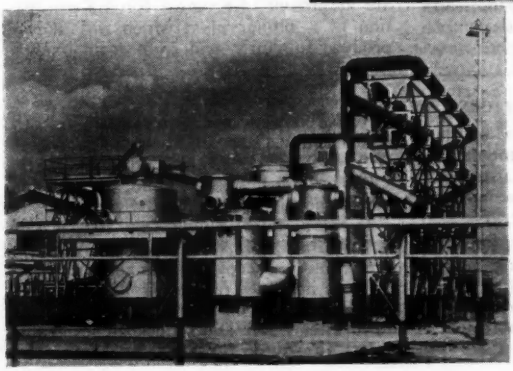
recently formed Swiss subsidiary company, the Société Continentale de Simon-Carves & Huntington Heberlein Londres S.A. with offices in Zurich.

The Nichols Freeman technique of flash roasting by pneumatically injecting a stream of finely divided pyrites directly into the combustion zone gives extremely rapid and efficient combustion and produces a gas containing about 10 per cent of sulphur dioxide by volume with a very low sulphur trioxide content. It also enables full advantage to be taken, by means of waste heat boilers, of the natural heat of combustion of the exothermic metallic sulphides, over 95 per cent of the heat liberated during combustion remaining in the gas passing from the roaster to the waste heat boiler. Steam at any pressure from 100 to 450 lb. per sq. in. can be generated at the rate of approximately three tons of steam per ton of equivalent sulphur burnt as pyrites, and it is stated, for example, that a plant roasting 50 tons of pyrites per day can produce about 400 h.p. in the form of electric power; this figure does not include the substantial additional power obtainable by applying waste heat recovery to the exothermic process of catalytic conversion in the actual acid-making unit. In large plants the total power available from waste heat recovery is more than sufficient to operate the flash roaster and acid plant combined, including all pyrites handling and grinding equipment.

From the economic viewpoint the large steam credit obtainable from this flash roasting technique is of obvious importance. The fact that the capital cost of a metallurgical plant, owing to its necessarily greater elaboration, is about double that of an equivalent sulphur-burning plant, and that waste heat recovery is not normally practicable with conventional hearth or kiln roasters, has always weighed heavily against the



Part of a double-unit sulphur-burning plant recently completed for Courtaulds, Ltd.



An outdoor sulphur-burning sulphuric acid plant in the Dutch West Indies for the Curacaoshe Petroleum Industrie Mij.

A 240-ton outdoor sulphur-burning plant for Fisons, Ltd., at their Immingham fertiliser factory

metallurgical plant in spite of the fact that sulphur is a more costly raw material than pyrites. The whole picture is substantially altered by the waste heat recovery made possible by flash roasting, which gives the metallurgical plant important additional operating economies to be set against higher capital outlay.

More recently Simon-Carves have concluded arrangements with the Badische Anilin- & Soda-Fabrik under which they can also supply their 'turbulent layer' roaster, which treats pyrites fines without grinding and can also handle concentrates with normal moisture content. After exhaustive preliminary work at the pilot stage, one Badische roaster unit is now operating very satisfactorily on the commercial scale, and further large-scale units are in course of construction.

The Kachkaroff process, which can be regarded as a logical development of the lead chamber process, depends on the oxidation of sulphur dioxide to trioxide in the presence of nitrogen oxide acting as a catalyst. By using a packed tower and a high nitrosity of the circulating acid it is possible to carry out the oxidation as a liquid phase reaction, resulting in a decrease in chamber capacity and nitre consumption. A distinctive feature is the extreme flexibility of the reaction, which allows of widely varying gas strength.

An important point is that the Kachkaroff process can make use of the spent oxide which is produced in large quantities at gas works and which cannot be used for sulphuric acid production in a contact plant. The first Kachkaroff installation in Britain is to be built by Simon-Carves at East Greenwich gas works for the South Eastern Gas Board, where it will treat spent oxide from gas works throughout the Board's territory. Negotiations with another client are at present in progress for the construction of a similar plant which will likewise produce sulphuric acid from spent oxide.

Fabricated Aluminium Prices

INCREASES in the selling prices of its fabricated products have been announced by the British Aluminium Co., Ltd., due to the effects of the rise in costs of raw material and recent wage awards.

As a result of the advance in the Ministry of Supply official price of virgin aluminium from £124 to £148 a ton, which came into force 1 January, 1952, it became necessary to increase the selling prices of fabricated products by 2½d. a lb.

Increases were (per lb.).—

Rolled products: Pure aluminium and B.A.60 alloy, ½d.; all other alloys, except D.T.D.68, 1d.; D.T.D.687, 2d.

Extrusions: Pure aluminium, ½d.; all alloys except the high zinc strong alloy group, 1d.

Tubing: Pure aluminium, 1d.; B.A.60, B.A.21, B.A.24, B.A.25, B.A.27, B.A.28, 2d.; strong alloys, except the high zinc group, 3d.

These increases ranging from 3d. to 5½d. a lb. take effect on all new orders received on or after 1 Jan. and on despatches against orders already on the books by 14 Jan.

Aromatic Hydrocarbons in Fuels

Method for Quantitative Determination

THE Belgian Ministère du Travail et de la Prévoyance Sociale, in its chemical Inspection Department, has lately introduced a new method for testing motor fuels and industrial solvents for aromatic hydrocarbon content, based to some extent on the relatively old methods of Marcusson that have in recent years been largely forgotten or ignored. The method is described by Dr. Stassens, chief chemist for the Ministry (*L'Ind. Chim. Belge*, 1951, **16** (9), 546-550). The author reviews several of the more recent and well-known analytical procedures, including a reference first of all to the qualitative physical test based on u.v. absorption (or Raman) spectra; and proceeding thence to discuss briefly the chemical methods of Hedrich Wells, J. Manning, J. Thole, Hess, Egloff and Morrel, Garner, etc.

Marcusson's method (*Zt. f. ang. Chem.*, 1931, **26** (11), 678) was found to be very accurate, and with some modifications has been adopted as the official test by the Ministry. Now that the quality of motor fuels is mainly gauged by their octane number, this particular analysis may have lost something in importance; but from a toxicity point of view it certainly cannot be ignored, and this applies of course to industrial solvents. Nitration, the first step, may be done in various ways, e.g., by introducing into a measured quantity of petrol or solvent fuming nitric acid (5 cc. per 10 cc. of test material), stirring carefully under a current of cold water and allowing reaction gas to escape. The mixture darkens somewhat but soon clears if sufficient HNO_3 has been used, though this does not matter very much in view of subsequent operations.

Mixture Separates

After stirring, the mixture separates into two layers, of which the lower—HNO_3 and nitrated aromatics—is passed into an Eggertz tube of 30 cc. capacity containing a little water. The upper layer is again nitrated once or twice with 2-2.5 cc. of fuming acid. About 10 cc. of acid is generally sufficient to nitrate all the aromatics present. The lower layers in these further treatments are also transferred to the Eggertz tube which is then stoppered, shaken, and placed in a vessel of 500 cc. cold water. Total volume of top layer of nitrated product is read. This reading may be facilitated by introducing a definite amount of toluol into the Eggertz tube. In this case the contents are made up to 30 cc. with water, and the tube closed and shaken carefully. The toluol aids separation.

Sufficiently Accurate

When thoroughly clear the volume of the top layer is read and after deducing that of the toluol the remainder is divided by 1.15. The quotient indicates the volumetric percentage of aromatic hydrocarbons present. The method is very rapid, and sufficiently accurate.

The author adds a few comments. There is no need for a cooling mixture or acetic acid as retardant. A preliminary try-out in a test tube with ½ cc. HNO_3 and ½ cc. of test material gives a useful hint as to the relative violence of the reaction and the probable content of aromatics. A density measurement is also useful beforehand. If excessive content of aromatics is apprehended the material should first be diluted with hexane, heptane, or de-aromatised benzine (petrol). The factor 1.15 has been proved by experiment to be generally accurate, the theoretical values being 1.16 for benzole, and 1.125 for toluol and xylol.

It is also necessary to consider the possibility of formation of dinitro derivatives, for which it is usually difficult to find the requisite correction factors or to obtain a precise idea of volume increase due to such derivatives. The author has calculated these values and found, for toluol, 1.27, and for benzole 1.36. But he thinks that all possible errors are compensated and presumably balance out, since experience has shown the factor 1.15 to be quite accurate. It is added in conclusion that the method is applicable also to many other solvents besides benzines and white spirits, but certain precautions are necessary in some cases; and it must *not* be used for chlorinated solvents, except possibly in the case of carbon tetrachloride. It is therefore recommended that denaturants used for benzines or other solvents should be Dammar gum or rubber rather than chlorinated solvents.

A Survey of Physical Chemistry

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ACTIVITY during the past year may be classified conveniently under the following headings: valency, molecular and crystal structures, hydrocarbons, macromolecules, reaction kinetics, colloid chemistry, adsorption and surface chemistry, electrochemistry. In a broad survey of the present dimensions it would be impossible to comment more than very briefly on all the contributions in these fields. The result would be little better than a reference list of the original literature. It has seemed more advisable, therefore, to indicate the trends of interest and development in certain of these subjects. It is not intended to imply that the topics discussed are ultimately of greater interest and importance than those excluded.

Period of Consolidation

In general, the period under survey has involved the consolidation of existing ideas and techniques rather than any fundamental change of outlook. In this respect there have been three main milestones: (a) publication of the contributions to the Royal Society Discussion on Bond Energies and Bond Lengths[1]; (b) the Faraday Society Discussion on Hydrocarbons[2]; (c) the Second International Congress of Crystallography at Stockholm[3]. As the writer was present at all three meetings, their themes and conclusions form the basis of much of what follows. As far as possible, however, an effort has been made to include, where relevant, references to recent work reported elsewhere in the literature. In addition, special sections are assigned to proteins and protein-like molecules, clathrate compounds, and tropolones, since these involve certain novel aspects which appear to have aroused particular interest. The various selected topics are treated under separate headings.

(a) *Valency*

While the term bond length involves little or no ambiguity, the same cannot be said about 'bond energy' which has often been used ambiguously and indiscriminately to describe two distinct magnitudes: (i) the mean contribution from each bond of a given type to the total heat of formation of the molecule from its constituent atoms; (ii) the energy required to disrupt the molecule at a particular bond into two fragments. The difference between these quantities has been analysed by Szwarc and Evans[4], who propose for them the terms 'average bond energy' and 'bond-dissociation energy' respectively. Knowledge of the 'average bond energy' requires unambiguous values for the heats of atomisation of elements, and these are not always forthcoming. This is still particularly true of carbon and nitrogen in spite of a large amount of experimental and theoretical investigation[5]. It is not surprising, therefore, that more and more attention has been given to the second quantity—the bond dissociation energy—where such problems do not arise. The present position and outlook on bond dissociation energies has been critically reviewed by Szwarc in the present year[6]. We now know for certain that the energy required to break a particular bond is not, as Fajans originally assumed, a constant characteristic of the bond and independent of the molecular environment. The kinetic methods developed by Szwarc[1, p. 5] continue to be most fruitful and interesting in this respect, and bond dissociation energy values have also been obtained by the thermochemical methods of Skinner and coworkers[7] and of Ubbelohde, Mackle and others[8]. These thermochemical values are a most important independent cross-check on the kinetic measurements, which involve a number of assumptions. The method of electron impact is also being applied as in previous years[9], and is referred to in more detail in section (c).

Bond Strength Factors

The factors which influence bond strength have been analysed by Walsh[1, p. 13] who has suggested a new definition of electronegativity. This quantity is defined by him for any atom A as the stretching force constant of the bond A-H, allowance being made in certain cases for repulsion between bond and lone-pair electrons. This new definition is the culmination of an analysis of the force constant data for diatomic molecules of the

type A-H[10]. It has been commented on by Linnet and Skinner[1, pp. 30, 31]. An alternative and more fundamental approach to the whole question of electronegativity is due to Moffitt[11]. Walsh has also put forward empirical relationships between force constants and ionisation potentials. These have had some measure of success in that they predict certain force constants satisfactorily. They appear rather *ad hoc*, however, and are subject to a variety of criticisms[1, pp. 30, 31].

In a paper on co-valency, electrovalency and electronegativity[1, p. 49] Cottrell and Sutton have helped to resolve the apparent contradiction between Pauling's adjacent change rule and Gordy's rule connecting electronegativities and bond strength. Their results also indicate that the importance of changes in internuclear repulsion is greater, and that of changes in ionic contributions is less, in causing the relative stabilisation of molecules with unequal centres, than has previously been supposed. They lead, however, to a similar expression for the stabilisation to that given by Pauling.

Sir John Lennard-Jones[1, p. 75] has reviewed recent theoretical developments in our understanding of the energies and bond lengths of conjugated molecules. The concept of π-orbitals forms the basis of the treatment, and has led to extensive and pretty successful calculation of resonance energies, percentage double-bond character, and bond lengths. A useful critical survey of the various approaches to the question of double-bond character, or, as it is more commonly called now-a-days, bond order, is included. This latter topic has been discussed in more detail by Coulson[1, p. 91], and the theoretical calculations compared with the results of X-ray analysis. Summarising briefly, it is fair to say that for hydrocarbons agreement between theory and experiment is fairly satisfactory (cf. Robertson[1, p. 103]). For heteropolar systems the position is not so good, and the development of methods for dealing competently with such molecules is one of the major current problems.

Molecular Orbital Theory

More recently, molecular orbital theory has been applied to the reactivities of conjugated molecules, and the results so far are promising (*e.g.*, [1, p. 122]).

From the valence bond point of view, the theory of ionic-covalent resonance has been discussed by Warhurst[1, p. 22], and the value of the method in the interpretation of experimental data on bond energies, bond lengths, dipole moments and force constants stressed. Despite its shortcomings, it is important to remember that the method of ionic-covalent resonance is the only one at present capable of dealing generally with bonds between unlike atoms. As was indicated earlier, this is a big defect of present molecular orbital theory.

Most Serious Criticism

The most serious criticism of the method of ionic-covalent resonance arises in the field of dipole moment calculations. One of the assumptions of the method is that the dipole moment of a pure co-valent bond is approximately equal to zero. This assumption has been attacked by Robinson, Coulson and others (*e.g.*, [1, p. 62]). It has been shown, for example, that μ_{co} HCl depends in a very sensitive way upon the *sp* hybridisation of the chlorine orbital, and 10 per cent *s*-character gives the experimental value of 1.1 D. However, although the nature of the hybridisation undoubtedly plays an important part, it has been shown recently by Warhurst and Whittle[12] that for HF at least, the observed dipole moment cannot be explained solely in this way. Ionic terms must be added to the wave function. The whole position requires considerable clarification.

The nature of directed valency continues to occupy attention, and an interesting paper has lately been published by Linnet and Poë on the directed valency of elements of the first short period[13]. The method outlined by these authors leads in many cases to conclusions different from the more usual wave mechanical approach. For instance, the interbond angles in NH_3 and H_2O would be expected to be but slightly less than tetrahedral, rather than ideal 90° angles deformed by electrostatic and other repulsions.

On the more experimental side, the nature of the co-ordinate link has been the subject of a series of papers by Chatt and co-workers[14], and it now appears that filled *d*-orbitals in a metal atom play a much more important part in general co-ordination than has hitherto been supposed. With regard to the occurrence of halogen bridge structures in co-ordination complexes, Chatt's work has demonstrated the presence of these in some platinum compounds, but Kabesh and Nyholm[15] have shown that their use with certain other metals requires care, and they

have suggested alternative formulations for such cases.

Following up an extensive compilation[16] of bond length data for molecules in the gas phase, Caunt, Mackle and Sutton[17] have redrawn attention to the problem of excessive shortening of bonds between fluorine and elements of the second short period. The inadequacy of the Schomaker-Stevenson rule and other attempts to describe this shortening is discussed.

Finally, the 'aromatic' bond and so-called 'aromatic' electrons have been the subject of particular experimental and theoretical interest. The general subject has been reviewed by Badger[18], and Brown[19] has reported detailed calculations of π-electron densities, mobile bond orders, resonance energies and spectra for several aromatic systems. McDonnell, Pink and Ubbelohde[20] have investigated experimentally the pseudo-metallic properties of potassium-graphite and graphite-bromine, and interpreted their results in terms of the bond theory of energy levels in graphite. The most important conclusion from these investigations is that the π-electrons are very markedly affected by the potassium or bromine atoms intercalated between the layers of fused aromatic nuclei.

(*b*) *Crystal Structures*

At the International Congress of Crystallography, held in Stockholm, 27 June-5 July, 1951, many interesting new ideas on the subject of crystal structure determination were described. None could be considered, however, as likely to revolutionise the subject. For structures with large numbers of parameters the established methods which make use of isomorphous replacement still remain supreme. The greatest advances in crystal structure determination involve the application of the Patterson synthesis, a method which, though now fifteen years old, is still providing fresh approaches. Difficulties arise in the interpretation of the Patterson function for complex structures on account of the large number of peaks. Four ways of resolving these difficulties have been discussed by C. A. Beevers[3], of Edinburgh University. The quantitative interpretation of Patterson functions with special reference to procedures such as modulation of the reciprocal space and systematic use of symmetry relationships has been described by Luzzati[2], of the Laboratoire Central des Industries Chimiques, Paris. M. J. Beurger[3], of M.I.T., Cambridge, Mass, U.S.A., has devised a new approach to crystal structure determination involving the application of vector set methods to the solution of the Patterson expression for the electron density. These are but representative samples of the developments and refinements in interpretation techniques. In all, thirty-seven papers were contributed on different aspects of this subject. Of particular interest to a later section of the present survey is the method of protein structure determination described by C. H. Carlisle, of Birkbeck College, London. It involves the interpretation of Patterson maps of protein crystals belonging to systems of low symmetry. Attempts at analysing such maps have been made on ribonuclease and chymotrypsin[21].

A Variety of Aids

On the more practical side a variety of mechanical and electrical aids are coming into general use in Fourier and structure factor computations, while the design of microphotometers for structure analysis continues to receive general attention. Geiger counter techniques are also being applied more and more to single crystal studies in order to improve intensity measurements. Recently an X-ray camera of rather elegant design, suitable for continuous recording of diffraction pattern-temperature diagrams has been described[22].

The elucidation of organic and inorganic structures and the study of transition point changes by X-ray methods continues apace. A few of the more interesting results in this field are briefly discussed in later sections.

The study of molecules in the gas phase by the diffraction of fast electrons has now achieved complete post-war re-establishment. New and considerably improved cameras have been described by Karle and Karle[23], Hastings and Bauer[24], Allen, Mackle and Sutton[25], Bastiansen and Hassel[5] and Bartell and Brockway[5]. Using the sector technique[26] in order to overcome the large intensity variation with scattering angle, more direct and precise interpretation methods may be applied, and these result in greater accuracy and far less ambiguous conclusions than was often hitherto possible. A large variety of interesting structural investigations have recently appeared in the literature[27] and others have been reported[5].

The use of microwave spectra in the determination of bond lengths and angles for the simpler molecules with permanent dipoles

continues to grow. The most recent survey of the subject appeared about a year ago[29], since when publication in the literature appears to have temporarily subsided.

Electric dipole moment measurements continue to provide much interesting information on the structure and electrical properties of molecules. In recent years quite an amount of attention has been given to the improvement of the methods of computation of moments[30], and Guggenheim[30] has lately claimed to have formulated a straightforward and lucid procedure which takes advantage of the more important features of the previous papers. On the experimental side Sutton and co-workers[31] have published an extensive study of polarisation in conjugated systems and several investigations of stereochemical phenomena[32]. Among other papers of interest are those of Le Fevre[33] and of Brown and De Vries[34]. The latter records the dipole moments of some important fluorine-containing organic molecules.

In the fields of infra-red and Raman spectroscopy a large number of investigations are reported. Activity generally follows the trends indicated at the Faraday Society Discussion of little more than a year ago[35]. Apart, however, from the recent very interesting use of polarised infra-red techniques in the elucidation of the structures of polypeptide and protein molecules (*see* later), no further details can be supplied within the space of the present survey.

(*c*) *Hydrocarbons*

A general discussion on hydrocarbons was held under the auspices of the Faraday Society in Oxford last April[2]. Several of the contributions covered similar ground to that already treated in section (a) of this survey. Thus, in his introductory paper, M. G. Evans stressed the importance of bond dissociation and activation energies. He drew attention to the marked contrast between the heats of homopolar dissociation of R-H bonds in hydrocarbons and their heats of ionic dissociation leading to the formation of carbonium ions[2,p.6].

At present, there appears to be no adequate explanation of the large differences between these quantities. A real need exists for a theoretical treatment of saturated molecules and radicals as adequate as that achieved for unsaturated systems. It may be that in the papers by Lennard-Jones, Pople and Hall[2,pp.9,18] there are the beginnings of such a treatment. One thing is clear: the structure and properties of even simple hydrocarbons will be understood a good deal better when more theoretical and experimental information becomes available on their ionisation potentials. The importance of this quantity in elucidating the electronic structure of molecules can hardly be overemphasised, as was recognised long ago by Mulliken[36]. Quantities like heats of formation, internuclear distance, and dipole moments depend on a *number* of occupied orbitals, and they yield but indirect information about *individual* orbitals. Ionisation potentials supply the key to such knowledge, and the experimental determination of these by electron impact methods is a growing subject, as is evident from the contributions of D. P. Stevenson, Schissler Thompson and Turkevich, and McDowell and Warren[2,pp.35,46,53]. At the present time the method, while obviously capable of yielding a lot of useful information, is beset by certain difficulties of interpretation, but the indications are that these may be ultimately tractable.

Potential Energies Problem

A problem which continues to occupy much attention is that concerned with the potential energies involved in rotations about single bonds. The majority of examples of this process investigated up to the present occur in hydrocarbon molecules. The theoretical problems which arise are of two general kinds: (a) the quantum mechanical and statistical thermodynamic inter-relationships involved in the potential energy function for internal rotation; (b) the origin of potential barriers in terms of the behaviour of the valence electrons of the molecule. These problems have been discussed by Pitzer[2,p.66] with special reference to the shape and height of the potential barriers in ethane and certain other molecules, and the present status of the entire problem has been surveyed by Aston[2p.73]. Other papers on these and related topics have been contributed by Oosterhoff and Hazebrock[2,pp.79,87], while the distribution of single-bond *cis* and *trans* isomers, 'frozen out' in the troughs of the potential energy curves for certain conjugated systems, have been investigated by Mackle and Sutton[37].

The 'crumpling' of flexible polymethylene molecules in the vapour phase has been studied by Ubbelohde and McCoubrey[2,p.95],

and it is concluded that such molecules are 'crumpled' or 'coiled' until the space occupied is about the same as for the corresponding *iso*paraffins. A moderate degree of uncoiling takes place on forming the liquid, but, as a rule, fully stretched molecules are only found in the crystal. Further evidence in support of these conclusions has appeared more recently[38]. The general bearing of such phenomena upon reactivity is a question of great interest.

Hydrocarbon Reactions

With regard to hydrocarbon reactions, these may be divided into two main classes: (a) thermal reactions, (b) oxidation reactions. The thermal decomposition of hydrocarbons involves simultaneously chain and purely molecular processes, and the kinetic relations in both are of great relevance to the theory of reaction velocity. This question has been discussed by Hinshelwood and Stubbs[2, p. 120] in terms of: the nature of radical chain reactions, the probability that the residual reaction after nitric oxide inhibition of chains is a molecular reaction, the rate-pressure law, the variation of activation energy with pressure, the relative probability of rupture of the carbon chain at various points, and the interpretation of experiments on the composition of products. The thermal stability and reactivity of hydrocarbon radicals has been studied by Szwarc[2, p. 143] in terms of bond dissociation energies, and the problem of the temperature-independent factors of radical reactions has been examined. An extensive study of the kinetics of the interaction of trichloromethyl radicals with cyclohexane has been reported by Melville and others[2, p. 154] and the kinetics of diene reactions at high temperatures have been described by Rowley and Steiner[195]. On the basis of very accurate measurements of ethane-ethylene equilibria and calorimetric heats of reaction, Kistiakowsky and Nickle[2, p. 175] have arrived at what is probably the most reliable value at present for the heat of hydrogenation of ethylene ($\Delta H = -32{,}600 \pm 50$ cals.). They also submit a value for the hydrogenation heat of propylene ($\Delta H = -29{,}850 \pm 50$ cal. at 298°K).

The oxidation reactions of hydrocarbons continue to occupy much interest, not only in themselves but also because of their value in applied fields. Of special importance is the part played by free radical peroxide carriers in low temperature oxidation processes. This question has been reviewed by Mulcahy, and a new theory for the low-temperature mechanism suggested [2, p. 259]. The influence of substituents on the ease of oxidation of hydrocarbons has been discussed by Hinshelwood in relation to theories of oxidation and general electronic theories of reactivity[2, p. 267]. New evidence relating to the combustion of hydrocarbons has been cited by Norrish, and older evidence reviewed[2, p. 269]. It appears that aldehydes are the most important intermediate agents of the chain-branching process. The kinetics of the iron- and copper-catalysed oxidation of certain hydrocarbon lubricating oils has been studied in detail by Brook and Matthews[2, p. 299], and a chain reaction mechanism proposed.

(*d*) *Proteins*

Of particular interest during the past year have been the reports of studies on the structures of large polypeptides and related protein molecules. The infra-red spectroscopic method has been widely used in the customary way in the diagnosis of residual units and characteristic groups. The value of such studies has been greatly enhanced by the controlled polymerisation and co-polymerisation techniques which have in recent years become available. By examining molecules of gradually increasing complexity a fairly comprehensive chart of characteristic frequencies for residues is now available. Previously it had been impossible to determine such frequencies, for, in smaller polypeptides, the end groups dominate the spectrum. Using these residue frequency charts it is quite easy to recognise the chief amino-acid residues present in complex protein structures, and a lot of interesting data along these lines have been reported in recent years chiefly by Sutherland and co-workers in the U.S.A.[39] and by Thompson's school at Oxford[40]. In the near infra-red region there have appeared in many cases not one, but two characteristic N-H stretching frequencies for the hydrogen-bonded system $CO \cdots H-N$. The origin of the secondary frequency at 3,050 cm.$^{-1}$ is not yet fully understood[41].

Of particular interest in the application of infra-red methods has been their very recent employment, chiefly by Ambrose, Elliott and Temple[42], in the study of the orientation and folding of polypeptide and protein structures. This has been possible because of the

considerable advances in the design of infra-red prism spectrometers[42], and by the use of polarised infra-red radiation. By controlling the direction of the electric vector relative to the chain axis of polypeptide and protein films and crystals, differences in behaviour for different directions of this vector may be observed. Ambrose and Elliott first studied in this way a film of the synthetic polypeptide, polyglutamic ester, and their results show that the N-H bonds tend to lie parallel to the chain axis. They may be explained if the polypeptide chain is folded. and maintained in the folded state by *intra*-chain hydrogen bonding. Further experiments have indicated a similar fold for α-keratin, α-myosin and α-tropomyosin, whereas in β-keratin the N-H and C=O bonds tend to lie perpendicular to the chain axis. the hydrogen bonding being *inter*-chain in type.

On the basis of their experiments, Ambrose and Elliott have suggested a new type of α-folding involving *two* residues. This differs from the Huggins-Astbury type of folding, which has *three* amino-acid residues per fold, and which is based on X-ray evidence. The α-fold of Ambrose and Elliott, however, finds independent support from the X-ray studies of Bamford and others[45], and it is becoming increasingly apparent that the evidence for the Astbury-Huggins fold needs careful re-examination. For instance, this latter fold involves *inter*- as well as *intra*-molecular hydrogen bonds, and this is not consistent with the solubility of such α-forms in solvents like $CHCl_3$ which are not powerful hydrogen-bond-splitting agencies[42].

An Important Difference

One important difference between the X-ray and infra-red methods of studying such structures is the following. X-ray studies give information only about the ordered crystalline regions of the fibres. They reveal little or nothing concerning the amorphous parts. Although they do not yield the same detailed information, the above infra-red techniques give knowledge about the *whole* material, and thus provide a very important addition, as well as a cross-check, to the results of the X-ray method.

A very thorough application of the X-ray method to the study of ribonuclease has recently been reported by Carlisle and Scouloudi (*see* section (b) also ref. 21). The main conclusion drawn from the Patterson projection maps favour a two-amino-acid residue repeat. The indications are that the ribonuclease molecule has a molecular weight of 10,000-13,000, and that it contains five parallel 'crystallographic' polypeptide chains arranged in hexagonal close-packing.

Further three-dimensional vector studies are necessary to determine the type of chain system that best fits the data.

Among the latest polypeptide chain configurations that have been proposed to account for the X-ray diffraction data in general are the helical ones of Pauling, Corey and Branson[46]. The views of these authors have been supported by the experiments and calculations of Perutz[47] and criticised by Bamford and Hanby[48].

The chemical statics and dynamics of proteins in solution have been discussed by Moelwyn-Hughes[49].

(e) *Clathrate Compounds*

Last April, H. M. Powell, of the Chemical Crystallography Laboratory, Oxford University, gave a discourse entitled 'Atoms Encaged'. The substance of this talk has subsequently been published[50].

For a long time crystalline addition compounds of quinol and a second gaseous substance like sulphur dioxide, hydrogen sulphide, hydrogen chloride, etc., have been known. In some the ratio of the second substance to quinol is less than 1: 3 but only with methanol and methyl cyanide does the ratio reach 1: 3, and this is never exceeded. The nature of these crystalline addition compounds was puzzling. There could be no bonds in the chemical sense and no great Van der Waals attractions because of the volatile nature of the second components. Why at ordinary temperatures was there no significant dissociation? What was the explanation of the usual 1: 3 ratio and its variations, and why did quinol choose certain companion molecules and reject others? Why at ordinary temperatures was their no dissociation and why in the series HOH, CH_3OH, C_2H_5OH, etc., was methanol alone singled out for such combination? Such were the questions to be answered. X-ray crystal structure analysis has done so.

The quinol structure is not a very close-packed one. It contains a set of cavities, each roughly spherical and of about 4 Å diameter. It is in such spaces that the molecules

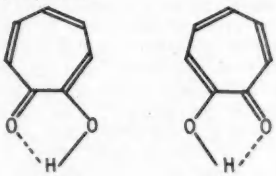
of sulphur dioxide or other substances which form these molecular compounds are trapped. The molecule once trapped cannot escape. As it approaches the walls of its cage large forces of repulsion between it and the walls are set up. There are no holes large enough to allow it to escape without coming much closer than the normal Van der Waals contact distance would allow. There are three molecules of quinol in the material of the cage structure for every cavity formed. This explains the 1 : 3 ratio mentioned above. It is a limiting composition since some cages may be left empty. The enclosed molecule must be small enough to go into the space available and large enough not to escape through the available holes. Ethanol is too large, water too small, which answers another of the questions above.

Powell is of the opinion that many such 'enclosure' compounds may exist and has given characteristic properties by which they may be possibly detected.

Because of their behaviour these compounds provide new and striking possibilities for preparing pure materials and for carrying out, through the difference in the geometrical form of their molecules, separations of, say, isomeric hydrocarbons. For example, such hydrocarbons might be separated by using their urea 'clathrates', as these compounds are called, for the straight chains fit into the honeycomb, but the branched ones cannot. Again, benzene of reasonable purity may be further rid of impurities like cyclohexane by formation of its nickel cyanide/ammonia clathrate, which is later separated and decomposed. It is thus obvious that, apart from their purely academic interest, clathrates have a practical significance worthy of exploitation.

(*f*) *The Tropolones*

Tropolones are a new class of compounds containing a so-called tropolone ring. This ring system was postulated a few years ago by Dewar[51] to account for the unusual properties of the mould metabolites stipitatic and puberulic acids and the alkaloid colchicine. The tropolone ring is of great interest from the theoretical point of view, since it represents a new 'aromatic' structure. The resonance stabilsation s high (28.6 k.cal./mole), but not as large as for the true aromatic systems[52]. The parent compound, tropolone, has a formula to which the resonance structure (1) and (2) make important contributions. The hydrogen of the 'olone'-group belongs to both atoms (hydrogen bond).



(1) (2)

Detailed spectrochemical investigations of a large number of tropolone compounds have furnished much evidence in favour of the planar structure of the tropolone nucleus and its general aromatic character[53]; and a determination, by X-ray methods, of the bond lengths has been reported by Robertson[54]. Kurita and Kubo[55] have carried out a molecular orbital treatment of tropolone in which the π-electron distribution, interatomic distances and dipole moment have been derived. The dipole moments of tropolone and some related compounds have also been determined experimentally by these workers[56].

One interesting fact about tropolone is that the bonds between the proton and the two oxygen atoms are not the same. The possibility of electronic resonance degeneracy involving two equivalent bonds is thus excluded. The indications are that there is a tautomeric oscillation of the proton, through a distance of 0.5-1.0Å, between the two oxygen atoms. The oscillation is slow compared with the vibration frequency of the O-H bond, and therefore does not confer appreciable resonance energy on the structure.

The antibiotic activity of β-methyltropolone has been studied by Elsden and Marshall, but their results have not yet been fully reported.

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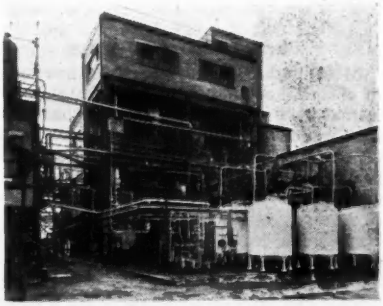
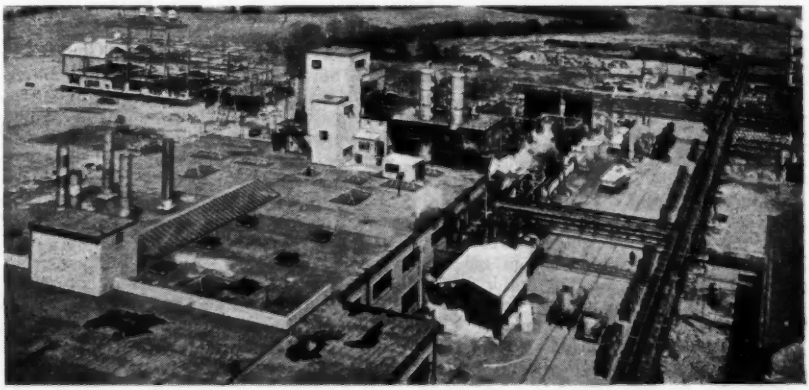
Monsanto's New Factory

Trade and technical Press representatives were given the opportunity to inspect Monsanto Chemicals new factory at Newport, in July

Exterior of the 'Aroclors' plant (right) which manufactures chlorinated diphenyls

General view of the 'Santomerse' building (below), the largest unit of the plant





Review of Safety and Fire Protection for the Year 1951

by ALEC WEBSTER, M.Sc., M.I.Chem.E., A.R.I.C.

IN writing a review of safety and fire protection for a chemical journal or, for that matter, any journal which covers a restricted field, one has to consider certain problems. First, whether information of a general kind which is only distantly connected with the industry concerned should be included, and second, to decide what represents an advance in the knowledge of the subject. For the first question, I shall take a broad view but, regarding the second, it is difficult to define an advance in the knowledge of safety or fire protection unless one considers it as something which may reduce the toll of damage to persons or property through either accident or fire. This seems to be a reasonable definition.

Chemical Safety Advances

Most of the advances recorded in respect of chemical safety might be termed negative in that they represent a discovery that some substance is toxic or that a particular chain of circumstances may produce a harmful result. These discoveries, unfortunately, usually come about as the result of an accident, but can be regarded as advances because the general principles of protection against the effects of toxic chemicals are well known and understood. Once the toxic or other properties of a chemical are known, it is not difficult to devise means to protect the operator until a more permanent form of protection (*i.e.*, alteration to the plant) has been found.

There is little to report that is new as far as protective devices are concerned. The writer visited one stall at the Shipping and Welding Exhibition and asked 'Are you showing anything new'. The answer was, 'Well, not really'. The types of applications of PVC fabrics is increasing, and it seems as if the teething troubles with the use of this material are being resolved. There have been some developments in types of goggles during the year, but nothing startling. This industry is highly competitive, and any developments appear quite quickly. The emphasis is on producing a goggle which will be comfortable, have a good field of vision and be well-ventilated. However good they may ultimately become, certain operatives will continue to wear them on the top of their heads and naïvely tell the safety officer that they are complying with the law. There were whispers early in the year of startling developments in the field of dust respirators, but so far they have been only whispers. There is room for advancement in this direction, but the problem is not at all easy.

There have been two quite important legal decisions during the year. The first, which went finally to the house of Lords, concerned the case of a disabled person who was almost completely unsighted in one eye. He was engaged in dismantling a motor vehicle and a sliver of metal flew from the chasis and entered the other eye, destroying its sight. The final judgment was, in effect, that the man was disabled and his disability made him be in a much greater risk of sustaining serious injury than a fit man doing the same work. His employers should, therefore, have taken special care to ensure that he was protected against such a risk even though the use of some form of protective device was not usual when doing his particular job. The fact that the man had been examined by the firm's medical officer caused them to be assumed to have full knowledge of his disabilities and heavy damages were awarded against them with costs.

Dermatitis Through Glue

The other case, which was quite different, concerns the case of a man who contracted dermatitis through working with synthetic resin glue. His employers used this material in two of the departments of their works. They supplied barrier creams in one but not in the other. The injured man had been transferred from the place where the cream was issued to the other one and developed a rash almost at once. In the judgment of the Appeal Court it was ruled that although the firm owed a duty to the man to provide him with protection the man, as he knew that a barrier cream which was in store would protect him and failed to ask for it, was guilty of contributory negligence. This

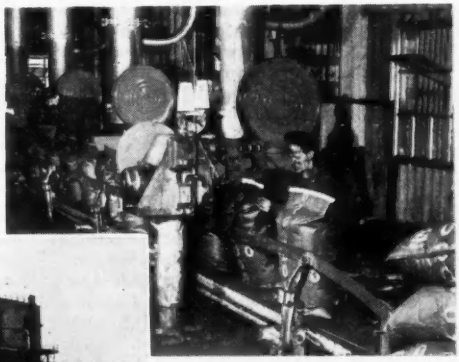
latter case is particularly interesting, as cases where an employee suffers through neglecting to use protective devices are rare. Although it is a statutory duty for an employee to wear protective devices in certain industries, most employers are reluctant to invoke this remedy.

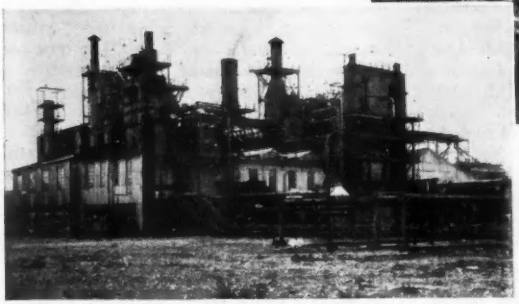
There have been very few published articles which may be regarded as the publication of original research on safety, although there has been a number of very useful contributions to our knowledge. The outstanding event has been the publication of Dr. H. E. Watts' book, 'Storage of Petroleum Spirit'.

In it the author draws on his unrivalled experience in this field. The appearance of such a book is long overdue as the scope of the Petroleum (Consolidation) Act and related legislation has extended enormously since the publication of a previous book on the same subject by Cooper-Key. This book explains the legislation and gives a great deal of useful guidance on all aspects of the subject. The author is at some pains to assure readers that the opinions expressed and suggestions made are his own personal views and are in no sense official, but very few people would question his opinions. This book may be well recommended to anyone who has to deal with the storage of products covered by the Act, or any other inflammable or hazardous liquid whether covered by the Act or not.

During the course of the year, several articles dealing with aspects of industrial safety have been prepared by members of the firms who actually make the articles described and who thus can draw on a wide field of experience. Although these articles are not directly concerned with the making or use of chemicals, they are of real value to anyone concerned with the operation of almost any type of factory. Two such papers—dealing respectively with ropes and chains—were read at the National Industrial Safety Conference at Scarborough and published in the Proceedings. The paper dealing with chains conveyed a large amount of information to the members, and in the other paper the speaker gave a clear description of the various types of rope in use at the present time—their advantages and disadvantages—from which it should not be difficult to decide what sort of rope to use for a specific purpose, and the material from which it should be made. A paper on 'The Safe Use of Caustic Soda for Enamel Stripping' (*Brit. Jour. Industrial Safety*, 1951, **2**, 3) shows how a distinctly risky process has been altered and developed into one which has been used without injury to any of the

During October Philblack's Carbon Black Plant at Avonmouth was visited by representatives of the Press





Above: The packing department and left: A general view of the plant

operators for over nine months. The alterations were simple and effective; *e.g.*, raising the tank above ground to ensure that the operators did not get splashed by leaning over the edge. The shaft carrying the chain wheel for operating the crane was extended to a length of about 12 ft., an additional rail being fitted on this account. The effect of this alteration is to ensure that the operator does not get splashed when entering or removing baskets of articles for treatment. This paper is very sound and contains many useful hints. In dealing with such problems, ventilation is very important as in some cases (*e.g.*, steel pickling) the vapours can be both inflammable and toxic.

Toxic Chemicals in Agriculture

Probably the most far-reaching report which has been issued during the year is the 'Report of the Working Party on Toxic Chemicals in Agriculture' (H.M. Stationery Office). This is a logical outcome of the 'Gowers Report on Health, Safety and Welfare in Non-Industrial Employment' (Cmd. 7664). It accepts the view that these chemicals will be with us for some time—possibly in perpetuity—and makes constructive suggestion for dealing with what is a major safety problem. Briefly, these are the supply of protective clothing and the recommendation that bathing and washing facilities be made available. It also suggests that spraying should not be done in windy weather, and that operators should be warned to keep on the windward side of the spray at all times. The recommendations are sound and in accordance with established practice in dealing with chemicals, but what the report does not tell us is how to make the sprayer wear the clothing in hot weather. This is one of the safety officer's major headaches.

The safe use of electricity and electrical appliances has not been forgotten. A new (Fourth) edition of the 'Memorandum by the Senior Electrical Inspector of Factories on the Electricity Regulations' (H.M. Stationery Office) has been published. The previous edition was issued in 1934 and the present one covers the scope of the new Regulations promulgated as the Electricity (Factories Act) Special Regulation, 1944. It fills a gap which has existed in our safety literature for far too long. As would be expected, the guidance is sound, especially on the user of low voltage portable tools. Mr. H. Midgley has written a paper on the 'Protection of Portable Electric Tools' (*Brit. Jour. Industrial Safety*) which is a description of the best methods of dealing with a difficult problem. These portable tools are very useful and their scope is widening. Unfortunately they are the cause of many accidents of which some are fatal. They are a source of anxiety to any safety officer. The author stresses the need for using these tools at a sufficiently low voltage to ensure that, should a user get a shock, he will not be injured. This again is the right approach; *viz.*, to recognise that the danger will be present and to reduce it to negligible amounts. It would be reasonable to assume that a shock received is a warning that the tool concerned is not in proper condition for use and if such a shock could be reduced to so small amount that it merely gives a 'Gentle Hint' that all is not well, such an arrangement would be a real advance in safety.

Turning to the purely chemical aspect of safety, some progress in knowledge can be recorded. An interesting example of direct and forceful action comes from Baltimore, Maryland. Statistics showed that during the last 20 years there have been 293 cases (83 fatal) of lead poisoning among children. The cause was mainly that the children picked flakes of paint from old woodwork and chewed them. The State has passed a new Housing Regulation banning the use of paint containing lead for the painting of the interior of any building (*Industrial Health Monthly*, 1951). In this connection it has been announced recently (*Chemistry and Industry*, 15 December, 1951) that the Minister of Food has approved the publication of a report recommending the introduction of limits for lead in food and drink.

Tartaric Acid Dust

An account has been published during the year of a case of serious dental erosion caused by tartaric acid dust. The dust concentration as estimated was 1.1 mgm./cu.m. The course of the attack was erosion of the enamel followed by attack on the dentine. The effect is similar to that caused by nitration acids. A report of this nature cannot help but be disturbing as in many cases compounds of similar constitution have similar dangerous properties. This instance suggests that the damage may be caused by acid conditions. An acid which is normally in the solid state would tend to adhere to the teeth, while the attack of

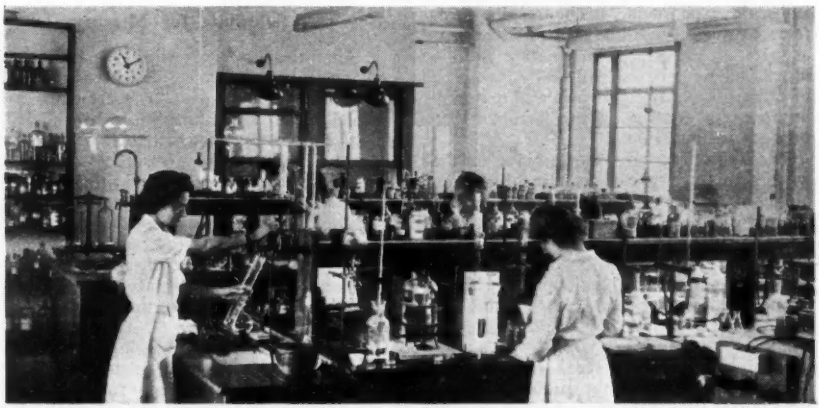
acid fumes would be transitory and so the effect of a solid acid might easily be more than its strength would lead one to expect. Cases of damage to teeth through the attack of chemicals are not often reported in safety literature, and it does seem that this report presents a very strong case for the dissemination of such available information for the benefit of safety officers. It is only by a wide spreading of information that the effects of dangerous materials can be minimised.

The Factory Department has issued a 'Memorandum on Carbon Monoxide Poisoning' (Factory Form 827). This is a new publication and is very good. Carbon monoxide still accounts for nearly 50 per cent of the reported gassing accidents and a booklet such as this, with its detailed study of the subject and the guidance it gives, represents a real effort to reduce the number of cases of poisoning. These Factory Department Memoranda are quite readable and interesting and one is led to think that they might with some advantage replace the statutory warning notices. An operative will often read a small book when he will not look at something headed 'Warning Notice'.

The use of N-Halogenimides as halogenating agents is on the increase and one fatal accident has occurred. Some reactions with these compounds are violent, as the particular case indicates. If a less dangerous compound can be substituted it seems clear that it should be, in order to lessen the risk to life and limb.

Safety and fire protection should go hand-in-hand and a number of the advances in fire protection have a decided chemical bias. 'Fire Research, 1950', the report of the Director of Fire Research, is a record of considerable progress. The major problems of fire research are big ones which take a long time to solve and the Department is dealing with these problems as they should be dealt with. In connection with the work on spontaneous heating, it has been found that a fire may be propagated by the burning of the fine hairs on the outside of the bags forming the stack. This means that a fire which starts in the centre of a pile of sacks and would on that account often be regarded as a case of spontaneous ignition, could be caused by the travel of a flame along the edges of the sacks from the outside. The Department has developed an apparatus on the lines of the Mackay Cloth Oil Tester except that it may be operated under definite conditions and this is to be used for studying the spontaneous heating of various substances. Such an apparatus will have a much wider application than the Mackay Tester.

An account of the risks of spontaneous ignition of spray-painting residues in spraying booths forms part of a paper by Dr. L. A. Jordan (*Chemistry and Industry*, 17



The new laboratories of the British Food Manufacturing Industries Research Association were opened during November. The main research laboratory is shown above

November, 1951). The suggestion is made that a water-backed spray booth would obviate this danger, and the suggestion seems an eminently reasonable one. The author points out that fires in these booths and the ducting connected with them generally take place at night when there is no current of air to keep the deposit cool, and on this account it would be better to have as much as possible of the ducting out of doors to keep it cool during the night. The effects, both intended and involuntary, which are brought about by spontaneous heating are so numerous that the correlation and co-ordination of the existing information is a formidable task which will take time, but will be time well spent.

Halogenated Hydrocarbons Disadvantage

The value of certain halogenated hydrocarbons as fire-fighting agents is well known and work is continuously being carried out on this subject. The disadvantage of these compounds is their toxic properties, not only of themselves but of the products formed when they are heated. Some of the fluorine compounds examined have proved less toxic than was expected, and some developments may take place along these lines. The discovery of a non-toxic hydrocarbon fire extinguishing medium would solve a great many problems.

Work has continued on the study of building construction in relation to fire prevention, and this has reached the stage of full-scale experiment. The results so far released suggest that the use of plaster board as part of the inside lining of a building instead of fibre board will delay the spread of a fire along a wall surface and materially improve the chances of the occupants getting out without injury.

The explosion which took place in 1950 when a mixture of carbon tetrachloride and aluminium powder detonated has focused attention on the active nature of aluminium powder. Tests have shown that a similar action can take place with other chlorinated compounds, and that the aluminium chloride formed acts as a catalyst. For some time, it has been known that it is possible to get a spark from a hot pipe painted with aluminium paint on a rusty surface. Several paints drawn from stock and not specially prepared have been tested to see whether sparking was possible. The general conclusion is that commercial oil-bound aluminium paints are quite safe unless heated to 150°C. or painted on a rusty surface. Sparks were produced with non-ferrous tools, which showed that it is no protection to use tools which claim to be non-sparking. This expression of opinion on a problem which has bothered a number of people is both timely and helpful. The chances of an explosion from such a cause seem rather remote.

The Association of British Chemical Manufacturers' Safety Conference dealt mainly with fire and explosion. Two papers were presented on fire hazards. They dealt with the hazards of the petroleum industry and with the manufacture of solvents respectively. The two papers were on very similar themes, but were different in the method of approach and were actually complementary to one another. They consisted of a description of methods which have stood the test of time and trial and form a useful part of the information on the subject. Dr. Firth discussed the 'Investigation of the Causes of Fires' and gave many examples from his own experience. He showed how in many cases the fire could have been not only prevented but avoided by the exercise of ordinary common-sense precautions. The examples quoted showed in nearly every case a complete disregard of certain matters which a true understanding of the process being carried out or the properties of the material used would have shown to be necessary. The Proceedings of the conference have been published.

Substitute for Mercury

An interesting suggestion has been made that tetrabromoethane could be used instead of mercury in measuring instruments provided adequate ventilation is provided. It is not generally known that at normal temperatures the vapour pressure of mercury is sufficient to produce a concentration which may produce toxic effects on continued exposure. The real need is for a non-toxic substitute for mercury and not one which is only less so. If this article refers to U-tube manometers, then the place where ventilation is required is where they are filled and not where they are used. The chance of a toxic concentration developing near the site of a mercury manometer is unlikely. The use of a toxic liquid for any form of specific gravity apparatus needs proper ventilation. If this is not provided, the method is open to adverse criticism.

A questionnaire on the requirements of the Factories Acts has been published (*Brit. Journ. Industrial Safety*, 1951, **2** (15), 16). This covers most of the legal requirements of these Acts particularly in respect of plant inspection and maintenance and the provision of guards, handrails, etc. Any 'Owner or Occupier' who can give the correct answer to all these questions need not view the visit of a Factory Inspector with any apprehension, as the list is very comprehensive.

Among the interesting devices which one has seen during the year is a gas burner which cannot be lit back even when a flame is applied to the air ports at its base. This was fitted to a domestic gas cooker and the effect is stated to have been achieved by a precise control of the air/gas mixture so that it is very near to the upper explosive limit. Such a device will need to be used with caution, as if the control is so precise it may be upset by a slight variation in the quality of the gas. It is however a step in the right direction. An electric heating mantle has appeared which can be said to be flameproof. This effect has been achieved by enclosing the heating wire behind a thin metal sheet. It is believed that this apparatus has received favourable comment from the Electrical Inspectors of Factories. The use of this form of apparatus is increasing and, if the makers' instructions whether detailed or general are followed, they are as safe or safer than most other form of heating where the temperature required cannot be obtained by steam.

Details of a method for prevention of explosions have recently been published. It is given in a paper by Glendinning and MacLennan in the *National Fire Protection Association Quarterly*, July, 1951. The proprocedure suggested is to fit diaphragms into the walls of the vessel containing the fuel. These diaphragms act as trigger valves which on an increase of pressure permit the discharge into the vessel of a sufficient amount of a fire extinguishing medium miscible with the fuel to prevent the explosion.

In preparing this review, an attempt has been made to point out some of the highlights and no one can realise more than the writer the number of omissions in it. When one realises that in 1949 there were 850 accidents or dangerous occurrences reported to the Factory Inspectorate from the chemical industry alone, which could be classed as being caused by chemicals as distinct from falls, cuts and bruises, etc., and that many of these were caused by something which was not previously known or understood and in which the finding of the cause, if properly used, represents an advance in safety knowledge, the many omissions may possibly be excused.

(*By courtesy of the 'Scotsman'*)

The 113th annual meeting of the British Association for the Advancement of Science was held in Edinburgh during August. The picture above shows the Duke of Edinburgh, the president

Fuel Economy & Use

Productivity Team to Visit U.S.A.

IMPORTANCE of the conservation and efficient use of fuel to Great Britain at the present time lends special interest to the departure for the U.S.A. at the end of this month of a specialist team to study American methods. This will be one of the series of tours sponsored by the Anglo-American Productivity Council with the technical aid of the Mutual Security Agency, which recently succeeded the Economic Co-operation Administration.

Wide-spread Interests

Nominations to the team have been made by bodies representing the engineering, heating and ventilating, cotton, woollen, brewing, chemical and paper industries in this country.

It should be noted that furnace industries and those depending largely on coal as a raw material (for example, iron and steel, gas, electrical power generation, pottery, and so on) are expressly excluded from the inquiry, and that domestic heating (as distinct from strictly commercial applications) will only be studied in so far as its demands impinge on the peak load of electricity supply undertakings.

Conservation of fuel being bound up with the original means of application of heat and energy, in whatever form except water power, the team's tour in America will take in power installations of diverse kinds in a variety of industries, besides firms manufacturing ancillary equipment, such as automatic control, the utilisation of exhaust steam through back-pressure generation and so forth.

Conferences will be held with various American associations in the realms of coal, gas and petroleum. It is anticipated that the report will formulate recommendations on the immediately pressing problem of economising existing resources, and also on a comprehensive long-term policy of fuel utilisation in this country.

A provisional list of members of the team, which will be under the leadership of W. L. Boon (Powell Duffryn Technical Services, Ltd.), includes:—R. H. Brennan (British Paper and Board Makers' Association, Inc.); J. H. Harris (Imperial Chemical Industries, Ltd.); E. G. Ritchie (British Coal Utilisation Research Association); F. W. Thomas (British Cotton Industry Research Association) and F. Wordley (Bradford Dyers' Association, Ltd.).

Chemical Merger in Australia

AMALGAMATION of their chemical interests in Australia has been announced by the Colonial Sugar Refining Company of Australia and the Distillers Company of Great Britain. The new concern, CSR Chemicals, Pty., Ltd., will manufacture cellulose acetate for rayon and plastic industries, acetic anhydride, and a broad range of industrial and pharmaceutical chemicals.

Capital of CSR Chemicals, Pty., Ltd., was recently increased from £A.3,000,000 to £A.6,000,000, and according to a statement by a spokesman for the Australian company full production was expected to begin by the end of this year.

Factories had already been built at Rhodes and in the Sydney metropolitan area. An acetic acid and cellulose acetate moulding powder plant and fine chemicals works had been completed.

In 1950 the CSR company had invested £500,000 in Courtaulds Australia, Ltd., and now supplied Courtaulds with acetone and cellulose acetate flake to produce acetate yarn.

Phthalate Price Changes

British Industrial Solvents, Limited, have announced that, following the recent rise in the price of phthalic anhydride, they are obliged to increase the price of 'Bisol' dimethyl phthalate, diethyl phthalate and dibutyl phthalate by 1½d., 1½d. and 1d. per lb. respectively for all categories of delivery, with effect from 1 January, 1952. For 5-ton lots, spot or contract deliveries over six months, carriage paid in returnable packages, the new prices are as follows:—

Dimethyl phthalate	2s. 0½d. per lb.
Diethyl phthalate	2s. 5d. „ „
Dibutyl phthalate	2s. 9½d. „ „

There will, however, be no change in the price of Bisoflex 81 and 82 (two dioctyl phthalates), while in the case of Bisoflex 791 and 91 the price has been reduced by ½d. to 2s. 9½d. per lb. for 5-ton lots, as a result of increased production of these plasticisers.

Some Recent Developments in Biochemistry

by K. R. REES, M.Sc.,
Department of Biochemistry, University College, London

THIS review, which covers the period October, 1950, to October, 1951, is restricted to those aspects of biochemistry concerned in the intermediate metabolism of carbohydrates, proteins and fats. No attempt has been made to review other important branches of biochemistry such as vitamins, hormones, comparative or clinical studies.

Carbohydrate Metabolism

Active acetate: The realisation that citric acid is an intermediate metabolite of the tricarboxylic cycle (T.C.A. cycle), has made the nature of the 2C compound taking place in the 2C + 4C reaction, of major interest in the last decade. Krebs originally proposed that the condensation product of pyruvate with oxalacetic acid (4C) was a 7C compound. Possible 7C intermediates were synthesised and found to be inactive. It was then suggested that citric acid was the condensation product, a decarboxylation of the pyruvate presumably having occurred. Results of isotope distribution studies of the T.C.A. cycle intermediates, however, had been interpreted to exclude a symmetrical molecule such as citric acid from being the original pyruvate-oxalacetate condensation product. A reinterpretation of the isotope experiments was therefore necessary, following the suggestion of Ogston (*Nature, 162,* 963, 1948) that a citric-acid-enzyme complex could be asymmetric. Experimental confirmation of this was soon forthcoming in the work of Potter and Heidelberger (*Nature, 184,* 180, 1949) with their demonstration that enzymatically synthesised isotopic citric acid could give rise to α-ketoglutaric acid which contained the isotope in only one carboxy group.

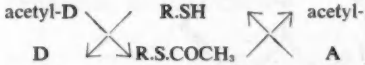
Lipmann (*Cold Spring Harbour Symp., 7,* 248, 1939) had found that acetyl phosphate is produced in the aerobic oxidation of pyruvic acid by extracts of *Lactobacillus Delbrückii.* The rapid destruction of acetyl phosphate in mammalian tissue by an extremely active acetyl phosphatase Lynen, *Ber. Deutsch. Chem. Ges., 73,* 367, 1940), made unlikely the possibility of acetyl phosphate being 'active acetate'.

In the last three years an increasing number of observations has shown that coenzyme A is a necessary co-factor in all acetylation reactions, e.g., acetylation of sulphonamide or choline. Stadtman (*Fed. Proc., 9,* 233, 1950) isolated an enzyme, referred to as transacetylase, from *Clostridium kluyveri* which appeared to catalyse a reversible transfer of the acetyl group of acetyl phosphate to coenzyme A. This evidence suggested that active acetate might be an acetyl derivative of coenzyme A. The presence of transacetylase was demonstrated in other bacteria, including *Escherichia coli* and *Cl. butylicum* (Chou, Novelli, Stadtman and Lipmann, *Fed. Proc., 9,* 160, 1950).

Synthesis of Citric Acid

The synthesis of citric acid was demonstrated by Stern and Ochoa (*Fed. Proc., 9,* 234, 1950) from acetyl phosphate and oxalacetate in the presence of bacterial transacetylase and 'condensing enzyme'. This latter soluble enzyme is present in a number of animal sources and has now been crystallised. This pointed to acetyl coenzyme A as the long-sought-for active 2C fragment. Lynen and Reichart (*Angewandte Chemie, 63,* 4, 1951) have isolated from bakers' yeast a substance possessing the biological properties of active acetic acid. With the addition of this active acetate it was possible to produce acetyl sulphonamide, in the presence of an enzyme, from pigeon liver without addition of further co-factors. The effective group of coenzyme A was an -SH group. This was a possible explanation of why *in vitro* studies of transacetylation had always required the addition of cysteine, which protected the -SH group of coenzyme A, and stopped its conversion to the inactive disulphide form.

Lynen and Reichert postulated the following mechanism for acetylation:



Acetyl donor Coenzyme A Acetyl acceptor

Further investigations by Stadtman,

Novelli and Lipmann (*J. Biol. Chem., 191,* 365, 1951) into acetyl transfer by a phosphotransacetylase system present in extracts of *Cl. kluyveri* and other bacteria, demonstrated the need for coenzyme A in catalysing the interchange of acetyl and inorganic phosphate and the arsenolysis of acetyl phosphate. The rate of arsenolysis was directly proportional to the coenzyme A concentration.

Studies of the chemical nature of coenzyme A by Baddiley and Train (*Abstracts of Papers Presented to the Chem. Soc.,* 1951) have resulted in the proposal of the structure for coenzyme A shown at the foot of the page.

These workers believe that a small unidentified group may be situated at position 2′ in the pantothenic acid part.

Stern and Ochoa (*J. Biol. Chem., 191,* 161, 1951) with soluble enzyme preparations from acetone-dried pigeon liver have synthesised citrate from acetate, adenosine triphosphate (A.T.P.), and oxalacetate, in the presence of coenzyme A and Mg or Mn as co-factors. Acetoacetate and other aliphatic mono-carboxylic β-keto acids can be substituted for acetate in the above system. A mixture of soluble enzymes from two sources—(a) *Escherichia coli* extracts and (b) a number of animal tissues or yeast extracts—actively catalyses the synthesis of citrate from acetate, A.T.P. and oxalacetate. The bacterial extracts contribute two enzymes which are needed for the formation of 'active acetate' from acetate and A.T.P. The tissue preparations, most of which lack the acetate-activating system, contain 'condensing enzyme'. This enzyme catalyses a reaction between 'active acetate' and oxalacetate to yield citrate. Some *E. coli* and other bacterial extracts also contain condensing enzymes. The suggested mechanism is:

(a) Acetate + A.T.P. $\rightleftharpoons$ (acetate-A.T.P. enzyme) acetyl phosphate + A.D.P.

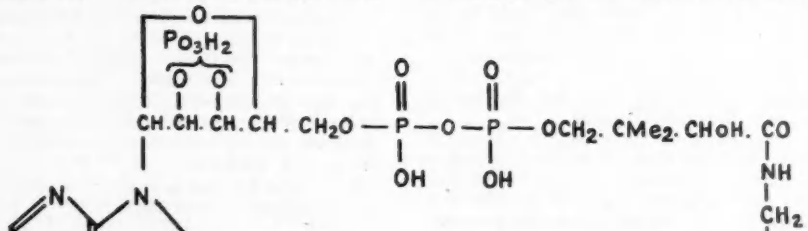
(b) acetyl phosphate + Co. A $\rightleftharpoons$ (transacetylase) acetyl Co. A + phosphate

(c) acetyl-Co. A + oxalacetate $\rightleftharpoons$ (condensing enzyme) citrate + Co. A.

Particulate Systems

Green has recently reviewed the activities associated with the Cyclophorase system in 'Enzymes and Enzyme Systems' (Harvard University Press, Ed. Edsall, 1951, and *Biol. Reviews, 86,* 410, 1951).

Schneider and Hogeboom (*Cancer Research, 2,* 1, 1951) have reviewed cytochemical studies of mammalian tissues and the isolation of cell components by differential centrifuging. It appears to be well established that the enzymatic activity of the Cyclophorase system lies in its mitochondrial content. These tissue particle preparations have been shown to contain most of the enzymes of the tricarboxylic acid cycle and also those which catalyse fatty acid oxidation. The range of enzymes associated with mitochondria is shown by the recent work of Schein, Podber and Norikoff (*J. Biol. Chem., 190,* 331, 1951) who, using differentially centrifuged rat liver homogenate, suspended in hypertonic sucrose, obtained evidence that most of the uricase activity of the homogenate was concentrated in the larger granules. Oxidation of many



of the tricarboxylic acid cycle intermediates by enzymes of these particle preparations is associated with an esterification of inorganic phosphate, *i.e.*, oxidative phosphorylation.

Judah and Williams-Ashman (*Biochem. J., 48,* 33, 1951) have used these enzyme preparations to study the effects of nitrophenols and related substances and of the two hormones thyroxine and insulin on oxidative phosphorylation. The hormones were found to have no effect on oxidative phosphorylation in these systems. The depression of oxidative phosphorylation by dinitrophenol (D.N.P.) was confirmed using a number of substrates. Judah (*Biochem J., 49,* 271, 1951) investigated the inhibition of pyruvate oxidation by D.N.P. in cell-free systems. It was found that A.T.P. or Coenzyme 1 (Co. 1), or added dicarboxylic acids of the tricarboxylic acid cycle, would bring about a reversal of this inhibition. There has also been a demonstration of the synthesis of A.T.P. from Co. 1 in such mitochondrial systems.

Enzymatic Cleavage

Kornberg and Pricer (*J. Biol. Chem., 191,* 535, 1951) have studied the enzymatic cleavage of Co. 1 with isotopic pyrophosphate. The reaction of nicotinamide with A.T.P., catalysed by specific enzymes in liver and yeast, has been shown to result in the production of Co. 1 and inorganic pyrophosphate (P.P.). Similarly, the reaction of riboflavine phosphate with A.T.P., catalysed by another yeast enzyme, produces flavine adenine dinucleotide and P.P. These reactions are freely reversible. Cleavage of the dinucleotides by P.P. results in the formation of A.T.P. and the respective mononucleotides. The hypothetical mechanism suggested is one resembling the reversible splitting of polysaccharides, disaccharides, and nucleotides by inorganic orthophosphate. The reaction is formulated as:

$$P^{32}P^{32} + \underset{\text{(Co. I)}}{\text{nicotinamide ribose P, P-adenosine}} \rightleftharpoons \underset{\text{(A.T.P.)}}{\text{nicotinamide-ribose P} + P^{32}, P^{32}\text{, P-adenosine}}$$

When studying oxidative phosphorylation (P/O ratios) one must add NaF (which presumably suppresses A.T.P'ase activity) to get appreciable phosphate esterification. Hexokinase and glucose are added to remove the A.T.P. formed. The enzyme systems involved in oxidative phosphorylation are unstable at room temperature. Kielley and Kielley (*J. Biol. Chem., 191,* 485, 1951) have shown that mouse liver mitochondria in isotonic sucrose solution possess little A.T.P'ase and A.M.P'ase (adenosine monophosphatase) activity. High rates of phosphate uptake were obtained with A.M.P. as external acceptor in the oxidation of α-ketoglutaric acid without fluoride and trapping agents. It is suggested that adenosine diphosphate (A.D.P.) is the primary phosphate acceptor and that myokinase is present in the mitochondria (probably all the myokinase activity is associated with the mitochondria). Barkulis and Lehninger (*J. Biol. Chem., 190,* 339, 1951) have shown that at high levels of fluoride (0.03M) the phosphorylation is impaired, whereas the phosphorylation of A.D.P. is undisturbed (at 0.01M fluoride no such differences in P/O ratios were found). The data suggests that the oxidative phosphorylation of A.M.P. is dependent on the action of myokinase, which is shown to be sensitive to a higher concentration of fluoride. Lehninger (*J. Biol. Chem., 190,* 345, 1951), using highly purified reduced coenzyme I (Co. 1 2H) has shown that the oxidative phosphorylation which occurs in the Co. 1-linked reaction, β-hydroxy butyrate $\rightleftharpoons$ acetoacetate, is associated with the oxidation of the Co. 1 2H. This paper also describes a method of preparing the barium salt of Co. 1 2H. Kennedy and Lehninger (*J. Biol. Chem., 190,* 361, 1951) demonstrated the activation of fatty acid oxidation by the oxidation of Co. 1 2H in washed particle preparations.

There have been numerous studies on the enzyme activity localised in fractions resulting from differential centrifuging of homogenates. Potter, Lyle and Schneider (*J. Biol. Chem., 190,* 293, 1951) have tried the effects of various fractions in various combinations on oxidative phosphorylation. It was found that the supernatant liquid from mitochondria contains an active adenylic deaminase which might cause a leak from the phosphate 'shuttle' system. The general opinion appears to be that the fractions should continue to be studied separately.

Tricarboxylic Acid Cycle

The presence of tricarboxylic acid cycle activity in numerous tissues of higher organisms is well established. Probably the main function of the cycle's activity in the higher organism is that of an energy-producing

pathway. Evidence is accumulating that the cycle also plays the part of a pathway in synthesis. This synthetic function may indeed be the cycle's major function in lower forms of organism such as the invertebrates, bacteria and fungi. Spiritus (*Fed. Proc., 10,* 250, 1951) demonstrated T.C.A. cycle activity in *Drosophila,* and Campbell and Stokes (*J. Biol. Chem., 190,* 835, 1951) in *Pseudomonas aereigenosa.* Massey and Rogers (*Aust. J. of Scientific Research, Series B.3,* 251, 1950) have also suggested that some form of the T.C.A. cycle functions in the tissues of certain Nematode parasites (*Nematodirus filicollis, N. spathiger, Ascoridae galli* and *Neoplectana glaseri*). Whether yeast possesses a T.C.A. cycle has been disputed for nearly a decade, but Foulkes (*Biochem. J., 48,* 378, 1951) has now definitely shown T.C.A. cycle activity in cell-free extracts of yeast.

Investigations of the individual enzymes of the tricarboxylic acid cycle have been investigated by a number of workers. Kornberg and Pricer (*J. Biol. Chem., 189,* 123, 1951) have demonstrated the occurrence of a Co. 1 and a coenzyme 2 (Co. 2)—specific *iso*citric dehydrogenases in both bakers' and brewers' yeasts. The Co. 1 specific form has an absolute requirement for A.M.P. and fails to catalyse the decarboxylation of oxalosuccinic acid. It also does not bring about the synthesis of *iso*citrate either from oxalosuccinate or from α-ketoglutarate.

Ackermann (*J. Biol. Chem., 189,* 421, 1951) studied the oxidative reactions of the T.C.A. cycle in relation to the production of the influenza virus. The functioning of the T.C.A. cycle of the hosts' cells is essential for the propagation of the virus.

An important synthetic function of the T.C.A. cycle is illustrated by the work of Shemin and Wittenberg (*J. Biol. Chem., 192,* 315, 1951) who have investigated the rôle of the T.C.A. cycle in the mechanism of porphyrin formation. Whole duck blood was incubated with acetic acid labelled with C^{14} in the carboxyl group, and acetic acid labelled with C^{14} in the methyl group. The haem resulting from each of these acids was degraded in order to locate the position of the isotopic carbon that originated from the acetic acid. The relative distribution of the C^{14} activities among the carbon atoms of the porphyrin can be explained by utilisation of acetate for porphyrin formation through a compound arising from the tricarboxylic acid cycle. This compound is not succinate, fumarate, malate, oxalacetate, pyruvate or acetoacetic acid, nor, if the α-ketoglutarate to succinate reaction is reversible, can it be α-ketoglutarate. The precursor utilised for pyrrole formation is thought to be an asymmetric 4C compound which can arise from α-ketoglutarate and succinic acid. It is suggested that this compound is a succinyl coenzyme complex formed either from succinate or from the oxidative decarboxylation of α-ketoglutarate. Possibly this coenzyme complex is succinyl Co. A. Green (*see* above, *Biol. Review,* 1951) has suggested such a complex as an intermediate in the oxidative decarboxylation of α-ketoglutarate.

Plant Tissues

In the field of plant tissues, Ochoa (*Fed. Proc., 9,* 551, 1950) has postulated reductive carboxylation

$$\text{Reduced Co. 2} + \text{Pyruvate} + CO_2 \rightleftharpoons \text{Co. 2} + \text{Malate}$$

as an intermediate step in a photosynthetic cycle, for example:—He considered that the photolytic split of water might be a source of hydrogen for the reduction of Co. 2. Supporting evidence that such mechanisms may play a part in the plant's economy is the demonstration by Ochoa and Vischniai (*Nature, 167,* 768, 1951) that a photochemical reduction of pyridine nucleotides by Spinach Grana and coupled CO_2 fixation does occur. Spectrophotometric and photometric studies by Mathews (*J. Biol. Chem., 189,* 695, 1951) in green peas show the oxidation of Co. 2 2H with methylene blue but not with ascorbic acid and oxygen. The oxidation of Co. 1 2H by oxygen and ascorbate did occur and was a cyanide-insensitive reaction.

Fructose Metabolism

Why fructose is present in two specific sites, *i.e.,* the male accessory organs and foetus of many mammalian species, whereas glucose is almost universally present elsewhere, still remains an enigma. In the case of sheep, Hugget, Warren and Warren (*J. Physiol., 113,* 258, 1951) have shown that the site of formation of foetal fructose is the placenta, and that the precursor is glucose. Parr and Warren (*Biochem. J., 48,* XV, 1951) have suggested that the mechan-

ism for the formation from glucose might be:

Glucose → Glucose-6-phosphate → Fructose-6-phosphate
alkaline ↓ phosphatase
Fructose

They have demonstrated the presence of such a phosphatase in the accessory sex organs of the rat, and Mann and Lutwak Mann (*Biochem. J., 48,* XV, 1951) have come to similar conclusions for bull seminal vesicles. Ainsworth, Parr, and Warren (*Jrn. Endocrinol, 7,* XIII, 1951) have considered the alkaline phosphatase content of various placental tissues, and demonstrated, in goat and sheep placentae—which form fructose—a much lower alkaline phosphatase activity than in guinea pig, rabbit, and rat placentae, which do *not* form fructose. These facts make it clear that the concentration of the enzyme is not the sole factor in determining whether the placenta from a species is capable of forming fructose from glucose.

Staub and Vestling (*J. Biol. Chem., 191,* 395, 1951) suggest that the primary phosphorylation product of fructose in the liver is fructose-1-phosphate. They have increased the purification of the fructokinase 6 to 10 times. Fructose-1-phosphate as the barium salt has been isolated as the principal phosphorylation product of fructose by the action of this enzyme.

One of the major difficulties in studying these problems is the lack of a method for the analysis of the intermediate forms. Walker and Warren (*Biochem. J., 49,* XXI, 1951) have suggested improvements in the filter paper chromatography of phosphate esters. It is also necessary to be able to prepare the intermediates. Seegmiller and Horecker (*J. Biol. Chem., 192,* 175, 1951) have introduced an improved method of synthesis of glucose-6-phosphate and 6-phosphogluconate based on a phosphorylation of glucose with polyphosphoric acids. Glucose-6-phosphate is converted to 6-phosphogluconate by the action of excess bromine over a period of 2 hours.

Alternative Pathways

A number of workers have considered reactions of the Warburg-Lipmann-Dickens scheme of glucose oxidation, leading to the formation of trioses by an alternative pathway to that of anaerobic glycolysis. Cohen (*J. Biol. Chem., 189,* 617, 1951) in *Escherichia coli,* Strain B, has investigated a magnesium-activated gluconokinase and the oxidative path of glucose-6-phosphate utilisation. Dickens and Glock (*Biochem. J., 50,* 81, 1951) have studied the direct oxidation of glucose-6-phosphate, 6-phosphogluconate and pentose-5-phosphate, by enzymes of animal origin, and the pathway described is shown to resemble closely that previously described for yeast. The authors of this paper also describe a useful preparation of Coenzyme 2.

Biotin

During the past 20 years a number of the B vitamins isolated have been shown to be intimately connected with enzymes, either as the prosthetic group of an enzyme, or as a structural unit of a respiratory catalyst. There have been a number of reports that the B vitamin biotin plays a part in carbon dioxide fixation in the animal organism. Ochoa, Mehler, Blanchard, Jukes, Hoffmann, and Regan (*J. Biol. Chem., 170,* 413, 1947) had observed that the activity of Ochoa's 'malic' enzyme was specifically and markedly reduced in the livers of biotin-deficient turkeys; reactivation could not be brought about by the addition of biotin. Blanchard, Korkes, del Campillo and Ochoa (*J. Biol. Chem., 187,* 875, 1950) showed an extremely active 'malic' enzyme to be present in *Lactobacillus arabinosus.* The enzyme is an adaptive one. Normal organisms require glucose and a medium for adaptation, whereas biotin-deficient organisms require biotin in addition to glucose and medium. Partial reactivation of the malic dissimilation system of biotin-deficient organisms occurs on incubation with both biotin and a small amount of growth medium. The reactivation requires glycolytic activity and proceeds very slowly in contrast with nicotinic-acid/nicotinic-acid-deficient organisms. The relationship of biotin to the enzyme systems of CO_2 fixation is less direct than that of a prosthetic group or of a component of a prosthetic group. It appears that biotin may be involved in the synthesis of these and possibly of other enzymes.

Studies on biotin-deficient animals had shown a decrease in ability to fix $C^{14}O_2$ into arginine; citrulline had also been observed to decrease in biotin-deficient rats. (CO_2 goes into arginine *via* citrulline and

ornithine, *see below*). Feldott and Lardey, (*J. Biol. Chem., 192,* 477, 1951) using washed residues of liver homogenates from biotin-deficient rats, found that the synthesis of citrulline from ornithine, with *l*-glutamate as a specific adjuvant, was greatly depressed compared with similar preparation from pair-fed controls. Replacing *l*-glutamate by carbamyl *l*-glutamate resulted in equal rates of citrulline synthesis by the biotin-deficient and control preparations. The decreased citrulline formation by the biotin-deficient preparation in the presence of glutamate was further inhibited by fumarate, oxalacetate, and aspartate. Under the same conditions these substrates were without effect on citrulline synthesis by liver preparations from the pair-fed control rats. The results indicate that the influence of biotin on CO_2 fixation into citrulline occurs in a step prior to that in which carbamyl-glutamate functions in the conversion of ornithine to citrulline.

Protein Metabolism

In the field of the intermediate metabolism of the amino-acids, attention has, in the main, been focused on the significance of transamination reactions. The narrow distribution and low activity of the *l*-amino oxidase isolated by Green, Nocito and Ratner had long thrown considerable doubt on the ability of this enzyme to account for the high rates of amino-acid disappearance that had been found. The past two years have brought the transaminase reaction into prominence in this connection.

Ingested amino-acids may undergo two fates in the mammalian body; they are either deaminated and then catabolised, the $-NH_2$ group being excreted as urea, or they are incorporated into the tissue proteins, either unchanged or in a modified form. In both of these cases transaminases appear to play a bigger part than had hitherto been supposed. In addition to the glutamic-pyruvic transaminase first reported by Braunstein and Kritzman, unequivocal evidence for a second enzyme has now been obtained by Tannenbaum and Shemin (*Fed. Proc., 9,* 236, 1950). They have showed that N^{15}-labelled leucine could, in the presence of a pig heart muscle preparation, transfer its $-NH_2$ group to α-ketoglutaric acid, as evidenced by the fact that the glutamic acid isolated from the system contained a high concentration of N^{15}.

It now seems highly probable that the two transaminases already mentioned are not the only two present in the body. The scope of the transamination reaction has been greatly widened by the recent demonstration of the probable existence of a whole range of such amino-group transferences. Feldman and Gunsalus (*J. Biol. Chem., 187,* 821, 1950) have shown that many amino-acids other than glutamic acid and leucine may take part in such reactions in bacteria, and last year Cammorata and Cohen (*J. Biol. Chem., 187,* 439, 1950) investigated the number of amino-acids participating in transamination reactions in animal tissues. Twenty-two amino-acids, apart from alanine, aspartic acid and glutamic acid, have been shown to take part. Herd and Rowsell (*Nature, 166,* 517, 1950), using chromatographic methods, also demonstrated the existence of a variety of transaminases in rat liver, showing that glutamate was formed when tryptophane, valine, leucine, histidine or glycine were incubated with α-keto-glutarate. They further showed that this reaction was catalysed by a washed preparation of the insoluble particles of rat liver homogenates, and presented evidence that this system was associated with the mitochondria. The reverse reaction, *i.e.*, the formation of amino-acids from the corresponding keto-acids, was also demonstrated.

Reaction in Animal Tissues

These papers emphasise the wide scope of the reaction in animal tissues, both from the point of view of amino-acid degradation, and amino-acid synthesis. Meister and Tice (*J. Biol. Chem., 187,* 173, 1950) have reported a similar reaction by which the δ-amino group of glutamine can be transferred to α-keto acids.

The importance of these reactions is underlined by the work of Nakada and Weinhouse (*J. Biol. Chem., 187,* 663, 1950) on the oxidation of aspartic acid. They have shown that the primary reaction is a transamination with α-ketoglutarate, as evidenced by an accumulation of glutamic acid. Subsequent oxidation of the aspartate was blocked by tricarboxylic acid cycle inhibitors, and they therefore suggest that the oxidation of aspartate involves a transamination with α-ketoglutaric acid and subsequent oxidation of the oxaloacetic acid so produced by the enzymes of the tricarboxylic acid cycle. The intrinsic interest of this

discovery lies in the fact that it probably represents a model of the oxidation of many amino-acids in the body. It also offers considerable support for the scheme put forward by Ratner (*Fed. Proc., 8,* 603, 1949) which integrates the individual steps in the aerobic transfer of nitrogen to form urea, with the transaminase system and the tricarboxylic acid cycle.

The formation of urea has also been intensively studied in the last two years. The ornithine cycle first proposed by Krebs has been greatly extended. Grisolia and Cohen (*J. Biol. Chem., 191,* 189-203, 1951) have shown that several stages are involved in the synthesis of citrulline from ornithine. Using $N^{15}H_3$, $C^{14}O_2$ and C^{14}-labelled carbamyl glutamate they were able to show that the carbon and nitrogen of the carbamyl group of the citrulline were derived from NH_3 and CO_2 added to the system, and not from the carbamyl group of the carbamyl glutamate. They postulated the following series of reactions:—

$$CO_2 + NH_3 + \text{glutamate} \xrightarrow[\text{triphosphate}]{\text{adenosine}} \text{carbamyl glutamate}.$$

$$\text{Carbamyl glutamate} + \text{A.T.P.} \longrightarrow \text{carbamyl glutamate}\sim P + \text{A.D.P.}$$

$$^3\ \text{Carbamyl glutamate}\sim P + NH_3 + CO_2 \longrightarrow \text{(intermediate)}.$$

$$^4\ \text{(intermediate)} + \text{ornithine} \longrightarrow \text{citrulline} + \text{glutamate}.$$

$$2CO_2 + 2NH_3 + \text{glutamate} + \text{ornithine} \xrightarrow{\text{A.T.P.}} \text{citrulline} + \text{glutamate}.$$

The scheme has been carried a stage further by Ratner and Petrack (*J. Biol. Chem., 191,* 693, 1951), who investigated the synthesis of arginine. They believe that two enzymes are involved in this step.

$$^1\ \text{Citrulline} + \text{aspartate} \xrightarrow{\text{A.T.P., Mg}^{\cdot\cdot}} \text{(intermediate)}.$$

$$^2\ \text{(intermediate)} + H_2O \longrightarrow \text{arginine} + \text{malate}.$$

Unidentified Intermediate

In neither case has the hypothetical intermediate been identified. The reactions described by Grisolia and Cohen appear to be catalysed by soluble enzymes, while those reported by Ratner and Petrack are catalysed by enzymes attached to the insoluble particles.

An interesting approach to the measurement of the actual rates of protein degradation and loss in the animal body has been made by Hoberman (*J. Biol. Chem., 188,* 797, 1950; *Yale J. Biol. Med., 22,* 341, 1950). Following the suggestion of Rittenburg (*Harvey Lectures, 44,* 200, 1949) Hoberman has used a method which depends on the previous enrichment of the body proteins with N^{15} and the subsequent measurement of N^{15} excretion. Among the treatments Hoberman has investigated are the effect of adrenalectomy, thryroidectomy, hypophysectomy and diabetes, and treatment with adrenocorticotropic hormone, pituitary growth hormone and 11-dehydrocorticosterone. He quotes figures giving the size of the metabolic pool of amino-acids, the rate of breakdown of protein and amino-acids and the rate of protein synthesis. In spite of the uncertainty of the postulates on which he bases his equations, and in spite of the fact that he has used glycine, which is an atypical amino-acid, this is an important contribution to our knowledge and techniques.

Group Transfer

Several papers have also appeared in the period under review which underline group transfer in protein metabolism. Perhaps the most important of these is the report by Hanes, Hird and Isherwood (*Nature, 166,* 288, 1950) on transpeptidation. The authors have demonstrated, by chromatographic methods, the block transfer of amino-acid radicals on to the γ-carbon of glutamic acid, found in glutathione, by incubating glutathione with a kidney enzyme preparation in the presence of leucine or phenyl alanine, with the subsequent hydrolysis and identification of a substance which appears to be γ-glutamyl-leucine or γ-glutamyl-phenylalanine. They stress the importance of this reaction and others related to it, as possible mechanisms involved in protein synthesis.

Another important contribution comes from the Fruton school. (Johnson, Mycek and Fruton, *J. Biol. Chem., 185,* 629, 1950; Fruton, Johnson and Fried, *J. Biol. Chem., 190,* 39, 1951). This emphasises that transamination reactions brought about by proteolytic enzymes at physiological *p*H may also be of importance in peptide bond synthesis since the exchange of the amino-acid on one side of a peptide bond can occur with little change of free energy, and they illustrate the point by describing the elongation of peptide chains by the action of papain and chymotrypsin. A point of

interest in this connection is the demonstration by Chantrenne (*J. Biol. Chem., 189,* 227, 1950) that coenzyme A is implicated in the formation of the peptide link between glycine and benzoic acid in the formation of hippuric acid.

Further reports have also appeared on the incorporation of glycine into nucleoproteins. Le Page and Heidelberger (*J. Biol. Chem., 188,* 593, 1950) treated rats with glycine labelled with C^{14} and found that it had been incorporated into the pyrine bases of desoxyribonucleic acid. The rapidity of this reaction casts some doubt on the accepted belief in the biochemical stability of this substance. The reaction has been further studied by Furst and Brown (*J. Biol. Chem., 191,* 239, 1951) who found different results when either N^{15} glycine or C^{41} adenine were fed to rats, and they suggest two mechanisms for the synthesis of the nucleic acids.

Biochemistry of Myosin

The biochemistry of myosin has continued to attract attention. Perry (*Biochem. J., 48,* 257, 1951) has investigated the adenosine triphosphatase activity of myofibrils isolated from skeletal muscle. Using an elegant method for the separation of rabbit muscle myofibrils by collegenase, he has demonstrated that the actomysin present accounts for all the adenosine triphosphatase activity. Spicer and Bowen (*J. Biol. Chem., 188,* 741, 1950) have shown that inosine triphosphate can cause the super-precipitation of actomycin if Mg++ is present. A.T.P. and I.T.P. are the only known substances that can do this. They have also showed that the reaction was not brought about by the amination of I.T.P. to A.T.P.

In this connection, mention must be made of the work of Bidinost (*J. Biol. Chem., 190,* 423, 1951), who used glycine labelled with N^{15}, or carbonyl with C^{14} and deuterium, to show that myosin and actin are regenerated less rapidly than is the average of the total muscle protein, a point of obvious interest in muscle physiology.

Finally, mention must be made of an outstanding advance in the purification of enzymes. Hitherto, those enzymes which have been associated with the particulate elements of the cell have resisted attempts to bring them into solution, and their purification has thus been rendered difficult. Morton (*Nature, 166,* 1092, 1950) has introduced the controlled use of n-butyl alcohol and has found that this enables ready solution of a wide range of enzymes, apparently by the removal of the lipid and other material by which they are attached to the cell structure. The method appears to have a wide applicability, and Morton reports the solubilisation and partial purification of many enzymes, including phosphatases, peptidases, dehydrogenases, transaminases, esterases and others.

Fat Metabolism—Absorption

Few papers have appeared on the absorption and transport of fat. Reiser and Bryson (*J. Biol. Chem., 189,* 87, 1950) and Chaikoff, Bloom, Stevens, Reinhardt and Dauben (*J. Biol. Chem., 190,* 431, 1950) have presented new evidence on the rate and route by which fatty acids are absorbed. The latter authors fed pentadecanoic acid-5-C^{14} and found that between 80 per cent and 90 per cent of it was absorbed. From 84 to 93 per cent of the absorbed material was recovered from the lymph and identified as a 15-carbon, C^{14}-labelled fatty acid. From this they concluded that the transport of long-chain fatty acids, both odd and even numbered, is by way of the lymphatics and that the length of the chain is not modified by the process.

Of rather greater importance is the finding of Reiser and Bryson that when C^{14}-labelled Δ-10,12-linoleic acid was fed, either in the free state or combined as triglyceride, then the labelled fatty acid was always found in the lymph, indicating that fed free fatty acids are absorbed by the same route as triglyceride. This is in direct opposition to the views of Frazer who maintains that while free fatty acids are taken directly into the portal system, triglycerides are, to some extent at least, absorbed in a particulate form and appear in the systemic blood. Bloom, Chaikoff, Reinhardt and Dauben (*J. Biol. Chem., 189,* 261, 1950) have also reinvestigated the nature of the absorbed fat in the lymphatics. They cannulated the thoracic duct and then fed C^{14}-labelled palmitic acid. Of the palmitic acid recovered from the duct 96 per cent was found in a form other than phospholipid and they suggest, therefore, that contrary to the views

of Sinclair, phospholipids play no part in fat transport.

Fat Metabolism—Oxidation

Weinman, Chaikoff, Stevens and Dauben (*J. Biol. Chem., 191,* 523, 1951) have provided new evidence of the occurrence of β-oxidation by injecting stearic acid, labelled either in the carboxyl group or on carbon atom 6, and collecting the respired CO_2 at intervals thereafter. Less $C^{14}O_2$ was recovered when the -6C^{14}- was injected than when the -C^{14}OOH was injected. They interpret this as showing that stearic acid loses two terminal carbons to give rise to palmitic acid, which then mixes with the body pool of palmitic acid before further degradation. The $C^{14}O_2$ produced from this derived palmitic acid will be only a fraction of the CO_2 derived from the degradation of the pool palmitic acid and this would account for the low respiratory $C^{14}O_2$. The nature of the two-carbon fragment produced by β-oxidation has been identified by Lynen and Reichert (*Angew. Chem., 63,* 47, 1951).

The past year has also seen several papers on the subject of acetoacetate formation. Most important of these was that by Stadtman, Doudoroff and Lipman (*J. Biol. Chem., 191,* 377, 1951) on the mechanism by which acetoacetate is formed. Their results show that the enzymatic synthesis of acetoacetate is not just an acetylation of the methyl group of acetate but requires the activation of the methyl as well as the carboxyl group. This reaction is envisaged as taking place by the 'head to tail' condensation of 2-acetyl $\sim$ CoA molecules to give rise to acetoacetate + 2 CoA. The origin of these two-carbon fragments is undoubtedly from the catabolism of long-chain fatty acids. Of great interest in this connection, therefore, has been the demonstration by Kennedy and Lehninger (*J. Biol. Chem., 185,* 275, 1950) that in their enzyme system they were able to achieve the oxidation, *in vitro,* of all the even-numbered fatty acids from 6 to 18 carbon atoms, saturated and unsaturated, and that not all of these acids produced proportionate amounts of acetoacetate; the shorter the carbon chain the greater the acetoacetate production; the longer the chain, the more CO_2 produced and the less acetoacetate. Essentially similar results were found by Weinhouse, Millington and Volk (*J. Biol. Chem., 185,* 191, 1950) and by Geyer, Cunningham and Pendergast (*J. Biol. Chem., 188,* 185, 1950), among others.

Several explanations have been put forward to explain this result, the most impressive of these being that elaborated by Kennedy and Lehninger (*Loc. cit.*). They return to the theory first put forward by Crandall, Brady and Gurin in 1949, that the two-carbon fragment derived from the methyl end of the carbon chain differs in reactivity from all other two-carbon fragments, and suggest that the usual two-carbon fragment has a high reactivity towards oxaloacetate, whereas the single two-carbon fragment from the methyl end may be relatively inactive toward oxaloacetate but very reactive in forming acetoacetate. Thus, in the short-chain fatty acids, in which this terminal two-carbon fragment constitutes a large fraction of the total two-carbon units produced, the tendency toward acetoacetate synthesis is maximal.

Asymmetric Distribution

This difference in the nature of the two-carbon fragment derived from the methyl end has also been used to account for the asymmetric distribution of labelled C^{14} atoms in acetoacetate when fatty acids labelled with C^{14} in the carboxyl group have been fed. Classical theory, *i.e.,* β-oxidation followed by random condensation of the two-carbon fragments so produced, predicts an acetoacetate molecule in which the $C^{14}O$: $C^{14}OOH$ ratio is unity. It has in fact been repeatedly shown that this is not the case (*see* Crandall, Brady and Gurin, *J. Biol. Chem., 181,* 845, 1949).

Two new theories have been put forward this year. The first, by Chaikoff, Goldman, Dauben and Gee (*J. Biol. Chem., 190,* 229, 1951) suggests that two separate mechanisms operate in acetoacetate synthesis. The first is random condensation of members of the 'two-carbon unit' pool, and the second a non-random condensation between the β-oxidised fatty acid residue and a randomised member of the liver two-carbon metabolic pool, followed by the oxidative removal of the terminal four carbon atoms to give an acetoacetate molecule. The relative proportions of these two routes would account for variations in the asymmetry of the C^{14}: $C^{14}OOH$ ratio. The first of these two mechanisms is believed to predominate.

A second scheme has been put forward by Green (*Biol. Revs., 26,* 410, 1951), which

also proposes two separate pathways for acetoacetate synthesis, and although the evidence on which this is based is unpublished and difficult to evaluate, nevertheless the scheme is ingenious and merits attention. It is important to notice that a new factor has been brought into this field by the demonstration of Plaut and Lardy (*J. Biol. Chem.*, *192*, 435, 1951) that CO_2 from the bicarbonate of the medium can be incorporated into the carboxyl of acetoacetate, and that this would have an important bearing on the occurrence of asymmetric labelling in the acetoacetate molecule.

During the past year further evidence has accumulated on the rôle of the Krebs carboxylic acid cycle in the complete oxidation of fatty acids to CO_2 and water. The necessity for the presence of intermediates of the tricarboxylic acid cycle to 'spark' the oxidation of fatty acids, *in vitro* (Kennedy and Lehninger, *Loc. cit.*), and the action of the tricarboxylic acid cycle inhibitors in reducing the production of CO_2 and substituting acetoacetate formation (Creyer, Cunningham and Pendergast, *J. Biol. Chem.*, *188*, 185, 1950), both point to the tricarboxylic acid cycle as being the pathway for the complete degradation of fatty acids.

In this connection the work of Kennedy and Lehninger (*J. Biol. Chem.*, *190*, 361, 1951) is of the greatest significance. They were able to show that in the presence of high concentrations of reduced Co. 1 (conditions under which coupled oxidative phosphorylation was known to occur), the oxidation of octanoate to two, and of palmitic to four, molecules of acetoacetate could be achieved, whereas when succinate (a Krebs cycle intermediate) was present less acetoacetate was formed and a greater part of the acid was oxidised to CO_2 and water. In the light of this work it is difficult to account for the observation by Fantl, Lincoln, and Nelson (*Biochem. J.*, *48*, 96, 1951) that 2-4-dinitrophenol had little effect on fat oxidation and their conclusion that oxidative phosphorylation was not involved in the intracellular degradation of octanoate.

The groups of workers under Folley and under Popják have continued their work on the biosynthesis of fats, particularly milk fats, and several papers have appeared from their schools. In the most important of these (*Biochem. J.*, *48*, 612, 1951; *49*, 610, 1951), Popják, French, Hunter and Martin injected $CH_3C^{14}OONa$ into a lactating goat and then isolated the even-numbered fatty acids of the milk. The distribution of isotope in the molecules clearly demonstrated that the long-chain fatty acids were built up by the elongation of short-chain fatty acids through the condensation of two-carbon units on to the carboxyl end, a reversal of β-oxidation. A similar conclusion was reached by Zabin (*J. Biol. Chem.*, *189*, 355, 1950), who found carboxyl-labelled stearic acid in rats treated with $CH_3C^{14}OONa$, and suggested that the stearic acid arose from the condensation of the acetate with endogenous palmitic acid.

A paper by Brody and Gurin (*J. Biol. Chem.*, *189*, 371, 1950) further underlines the great reactivity from the synthetic point of view, of the two-carbon fragment derived from fat catabolism in the formation of cholesterol and fatty acids. The same point has been made by Popják and Beeckmans (*Biochem. J.*, *47*, 233, 1950), who also demonstrated lipid synthesis from acetate in the extrahepatic tissues.

Professor E. C. Dodds, M.V.O., M.D., D.Sc., Ph.D., F.R.C.P., F.R.I.C., F.R.S., who was awarded the Medal of the Society of Chemical Industry on 11 July. Professor Dodds is Courtauld Professor of Biochemistry at the University of London. He is internationally known for his work on synthetic stilboestrol and insulin

Drugs, Fine & Medicinal Chemicals During 1951

by G. COLMAN GREEN, B.Sc., F.R.I.C., A.M.I.Chem.E.

AMONG the publications of 1951 concerning the pharmaceutical industry there are three notable ones. There is, first, the first edition of Volume No. 1 of the International Pharmacopœia which has suffered so long a gestation; second, there is the Productivity Team Report on Pharmaceuticals issued by the Anglo-American Council on Productivity; and, third, there is the 1951 Addendum to the British Pharmacopœia of 1948.

The International Pharmacopœia will be reviewed in an early subsequent issue of this Journal.

The report of the productivity team is so important to the industry that it is worthy of some detailed consideration over and above that already accorded to it (CHEMICAL AGE, 1951, **65** (No. 1,678), 317). This report can be of high educative significance provided that comparisons are made and conclusions drawn in proper perspective in relation to the differing scenes of U.S. and U.K. economies and commercial patterns. The oft-repeated basic fact must be firmly borne in mind that, in America, the pharmaceutical trade, in common with other trades, has a ready-made mass market 'on its doorstep'. This market is not only larger than the British home market on a proportional population basis but, as the Report reaffirms, it is effectively much larger than would be expected on a proportional population basis. This follows from the high purchasing power of the population in the U.S.A. and its great susceptibility to medication which has been established in earlier surveys ('The General Report of the Pharmaceutical Survey, 1946-1949'; American Council on Education, Washington, D.C., 1950; 'The Prescription Study of the Pharmaceutical Survey', J. Solon Mordell, American Council on Education, 1949).

This situation, combined with the highly competitive outlook of the people, leads inevitably to the necessity for highly efficient, mass-production methods which, in the pharmaceutical trade, implies large, continuous runs or large batch-scale operation according to particular circumstances. The

(*Courtesy, The Norwich Pharmaceutical Co.*)

A modern American pharmaceutical research laboratory

very high capacity of the market to consume depends ultimately on high remuneration for employees at all levels and this, in itself, demands large-scale, large-batch, highly mechanised and efficient runs adequately to absorb the high labour cost and salary overheads. Whether the high remuneration chicken or the high purchasing power egg comes first must be left to the debate of economists; but one imagines the situation develops logically, inevitably and initially from the large population and the relatively free play of private enterprise.

Economical Batch Sizes Stressed

These general considerations react fully on the pharmaceutical industry, a fact which is brought out early in the report (p. 4-5). There is confirmation in the passage stating: 'In the preparation of production schedules the highest importance is attached to the determination and maintenance of economical batch sizes in production, much more so than in British factories'.

The stake in the rich pharmaceutical market is such that, in order to maintain a place, the cost of research is on a commensurately large scale.

A further necessity to support this intensive scale of operation is the moulding of an appropriate organisation to succour it. The differences between U.S.A. and U.K. practices which consequently follow are most adequately summarised in the report when it says: 'The British tendency in factory management is towards economy of staff, wide fields of responsibility and simple problems of co-ordination. The American tendency is towards lavish use of staff, narrow fields of responsibility, many specialists and complex problems of co-ordination.'

With a slight practical acquaintance with the American pharmaceutical industry the present writer is of the opinion that each system has its weakness. The British system is likely to lead to a dilettantism leading to a gradual retrogression in commercial efficiency; the American system to a paralysing lack of flexibility and adaptability to changing circumstances. A certain amount of organisational flexibility is essential in British pharmaceutical practice in order to meet the varying demands of international trade and the writer is aware that Americans are envious of this flexibility when it comes to overseas trading. It is doubtful whether either system could survive unchanged in the *milieu* of the other.

The writer is in agreement with one passage in the report which states that there exists 'a greater tendency to produce specialists in narrow fields of activity. While this has short-term advantages, it leads to the production of technicians and managers with less breadth of experience or appreciation of the overall pattern of production than would normally be acceptable in British industry'.

Undoubtedly, each system has something to learn from the other. Much is revealed in the report which is of consequence in America and is so here with changing degrees of emphasis. Cost control is not new to British industry; but it does not permeate the whole organisation, from top to bottom, as the writer confirms is the case (p. 9). The achievement of higher productivity by the shedding of less profitable items and the concentration of a firm's resources on a narrow range of products (p. 11) is far from new to the British pharmaceutical industry. The problem is to know how far such an ideal can be pressed in the absence of a large mass-market and with established goodwill residing in what may be comparatively less profitable products in either home or diverse overseas trade. A too ruthless pruning can destroy a fruitful tree.

We have long envied the ready availability of plant equipment and packaging material in the States. But despite the apparent advantages enjoyed the team were impressed by the relative paucity in spectacular packaging developments and we may, perhaps, console ourselves that the extemporisations which are forced upon us in Britain are, in the long run, sufficiently spectacular in themselves and good for our national soul.

Pharmaceutical Processing

Chapter 5 of the report deals with 'pharmaceutical processing'. There is a notable lack of mention of statistical methods of quality control reflecting what is confirmed to be a much lesser awareness in American pharmaceutical industry than even that comparatively low level existing in the pharmaceutical industry of this country. What is revealed of pharmaceutical processing is of orthodox character and American methods are characterised, in the main, by high rates of output and the necessary adaptations to achieve this.

It is a pity there is no chapter dealing

with fine or medicinal chemical manufacture to provide a yard-stick for British pharmaceutical practice. The omission is a notable one since it is the foundation of the industry. This aspect was, one supposes, outside the terms of reference of the team and, indeed, it would have been straining the generosity and open-heartedness of our American friends to have requested its inclusion. Perhaps this gap has been provided for in the surveys of the German pharmaceutical industry published since the war finished (for example, 'The Pharmaceutical Industry in Germany During the Period, 1939-1945'; BIOS Surveys No. 24; HMSO, 1950).

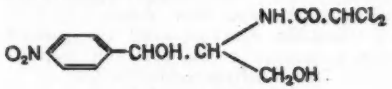
It is clear that the recommendations of the Pharmaceutical Productivity Team cannot be applied to British practice *in toto* nor is it recommended in the report. But it is clear by implication, that every British pharmaceutical firm should reconsider its own organisation and operations against the body and conclusions of this report in order to ascertain what part might be absorbed wth advantage.

In a Nutshell

One writer ('*Facts for Industry*', 1951, *4* (11), 10) puts the facts in a nutshell when he says that the numerous productivity teams which have toured America all reveal that there are clearly elucidated underlying factors related to America's economic efficiency. '. . . . if there were no such factors, the American companies operating in this country would long since have put British competitors out of business and, conversely, British companies would have failed to establish themselves in the States. When Lewis Ord made this point many years ago, he credited all America's commercial superiority to its retention of competition and blamed Europe's relative decline on restrictionism. No doubt it was an oversimplification, but none of the productivity teams has discovered a more convincing explanation'.

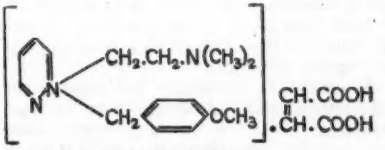
The third publication to which reference must be made is the 1951 'Addendum to the British Pharmacopœia, 1948', which is made necessary by the generally rapid advance in therapeutics since 1948. The principle changes to the Pharmacopœia made in this addendum relate to revision of monographs on penicillin and on certain biologicals. New monographs have been included which cover a group of antibiotics, synthetic drugs, and human blood preparations. It is impossibile to consider all the changes in detail here. There are a number of points worthy of general comment, however.

The inclusion of chloramphenicol (chloromycetin), the first synthetic antibiotic, is noteworthy. Its peculiarity as a naturally occurring substance containing a free nitro group and a chlorine atom has been discussed in earlier annual review numbers of THE CHEMICAL AGE.

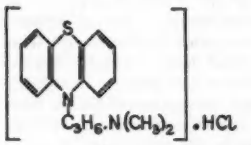


Chloramphenicol

The inclusion of monographs referring to only two of a wide range of available antihistaminic drugs is strange; but it is easy to appreciate that, if a start is to be made in providing standards for this group of therapeutic agents, mepyramine maleate (N-*p*-methoxybenzyl-N′ : N′-dimethyl-N-2-pyridylethylenediamine) and promezathine hydrochloride — (N-(2-dimethylamino-*n*-propyl)-phenothiazine should be chosen on account of their wide usage, availability and knowledge of their therapeutic characteristics.

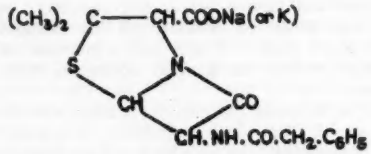


Mepyramine maleate



Promezathine hydrochloride

The amended penicillin monograph permits the use of the potassium salt of this antibiotic acid whereas, formerly, provision was made for the sodium and calcium salts only. 'Penicillin G' is promoted to a monograph of its own entitled 'Benzylpenicillin'. Its structural formula is quoted as:



Potency is to be determined by biological assay; but, in addition, the ratio of benzylpenicillin to total penicillins present is established by first determining total penicillins iodometrically and then determining benzyl penicillin gravimetrically (in parallel with a standard benzyl penicillin preparation) as the N-ethylpiperidinium salt.

Procaine Penicillin

Procaine penicillin also achieves a separate monograph but no guidance is given as to the preparation or formulation of this important agent for injection, although such is greatly needed because of the variable degree of efficacy of the injection according to the physical characteristics of the salt and the character of the suspending medium.

The monographs on bacterial vaccines and antitoxins have been considerably overhauled. The changes follow, in part, a change in the value of the International Unit for tetanus toxin, the introduction of aluminium phosphate-precipitated purified toxoid for diphtheria prophylaxis and, in part, to various improvements in processing technique such as the concentration of antitoxins by enzyme treatment.

A series of appendices are models of succinctness; and, indeed, they may, in some instances, prove to be disadvantageously terse, as, for example, Appendix XII dealing with the determination of water by the Karl Fischer method. The technique, in this instance, is not simple and the appendix will be of little guide to the novice who will require to read more widely before attempting the use of the method. A brief bibliography would be supremely useful here as elsewhere in the Pharmacopœia and its Addendum.

During the past twelve months the most notable developments have occurred in the corticosteroid field. The concentration of endeavour therein matches, if it does not actually exceed, that displayed with regard to antibiotics during the first few years after Florey's development of Fleming's original discovery of penicillin. At least the work on corticosteroids is not hampered by security requirements and lack of publication facilities which attended the development of penicillin in the war years.

In the short time since the announcement by Hench and Kendall, in 1949, that cortisone exerted its now well-known dramatic effect in the relief of symptoms of the crippling disease, rheumatoid arthritis, an enormous amount of ground has been covered, firstly, in appraising the therapeutic status of cortisone in respect of a wide range of complaints, especially those involving the collagenous tissues, and, secondly, in the study of the diverse physiological and pharmacological issues which the increasing (though insufficient) availability of cortisone and adrenocorticotropic hormone (ACTH) has opened up.

The reader who is less familiar with the field is briefly reminded that cortisone (11-dehydro-17-hydroxycorticostorone), known formerly as 'Compound E' is a ketosteroid normally secreted by the cortex of the suprarenal gland which lies adjacent to the kidney. Cortisone is one of a spectrum of steriods secreted by the gland. ACTH, however, is excreted by the anterior pituitary gland which is attached to the base of the brain. ACTH is a protein-like substance which has, *inter alia*, the property of activating the adrenal or suprarenal cortex to secrete corticosteroidal hormones including cortisone. Li has shown that the activity of ACTH lies in a peptide grouping and this may throw some light on the mechanism of action and lead to the elaboration of simpler substances with ACTH-like activity. After a wide search among the steroids only ACTH and cortisone itself evidence the activity of the latter—the first through its mediating action on the adrenal cortex and the latter because its effect appears to be quite specific to its structure.

ACTH Hard to Standardise

ACTH is only effective by injection and is very difficult to prepare in a pure form and to standardise. It is especially difficult to rid it of unwanted other anterior trophic hormones and of posterior pituitary hormones. On the face of it ACTH is more economical to use than the scarcer cortisone: but it has to be remembered in the first place that actions are not quite identical and, in the second place that, since ACTH supply depends upon the supply of hog pituitary glands, its supply is limited.

Since the pituitary gland and, therefore,

ACTH, has a mediating action on the adrenal cortex its action is entirely dependent upon the existence of an actively functioning adrenal cortex. In this connection it is a point of interest that the administration of cortisone tends to cause what need not be more than a temporary atrophy of the adrenal cortex and present thinking is that ACTH should be administered simultaneously or, at least, when cortisone treatment ceases (Claxton, *Lancet*, 1951, *ii*, 589) to stimulate the secretion of endogenous cortisone in adequate amounts.

Tests for adrenocortical activity, as well as of the efficacy of ACTH treatment, depend upon the estimation of the 17-ketosteroids and 11-oxysteroids in the urine, the detection of the reduction of circulating eosinophils (white blood corpuscles stainable with eosin) in the peripheral blood and upon other changes of a biochemical character which occur with less regularity.

Steroid determinations in body fluids are not a simple matter and the Medical Research Committee on Endocrinology offers a proposed standard method of 17-ketosteroid estimation (*Lancet*, 1951, *ii*, 585). The proposed standard method is based on those of Callow and Zimmermann and depends upon the development of a red colour with *m*-dinitro-benzene in alkaline conditions with compounds containing active methylene groups. This grouping is also found in the sex hormones and either androsterone or dehydroepiandrosterone is used as a standard in the estimation.

Colour Reaction for Steroids

Porter and Silber (*J. Biol. Chem.*, 1950, *185*, 201) describe a quantitative colour reaction for cortisone and related ketosteriods using phenylhydrazine in acid conditions. Biological fluids may require solvent extraction and other preparation to remove interfering substances. Zaffaroni *et al.* (*Science*, 1950, *lll*, 6) offer a paper partition chromatographic method for the analysis of adrenocortical hormones and outline a chromatographic method for their estimation in urine.

ACTH has been admitted to 'New Non-Official Remedies' during 1951 (*J. Amer. Med. Ass.*, 1951, *147* (4)). Provision is made for biological assay by measurement of adrenal ascorbic acid response in hypophysectomised rats (*i.e.*, rats in which the pituitary gland has been removed so that any adrenal response is of exogenous origin). The response achieved is compared with that obtained by the use of a standard preparation with the specific adrenocorticotropic activity of 1 mg. of the International Standard adopted by the World Health Organisation. This standard and the U.S.P. standard are identical. The test is based upon the fact that hypophysectomy causes rapid depletion of the ascorbic acid content of the adrenal gland (as well as other tissues such as plasma) whereas administration of ACTH helps to restore the condition to normal.

Cortisone acetate has, also, been admitted to New and Non-Official Remedies and the relevant monograph provides an excellent summary of its action and uses (*J. Amer. Med. Ass.*, 1951, *146* (15), 1422). Tests are described for identity, purity, and properties and dosage forms are described. Assay is by optical density methods with light at prescribed wavelengths.

'Wonder Drug' to 'Glorified Aspirin'

During 1951, a number of reviews have sought to place the position of cortisone in medicine in proper perspective. Whereas cortisone was formerly hailed by the popular science writers in America as 'The Wonder Drug', with the deflation of falsely raised expectations its status has tended to be diminished to that of 'A Glorified Aspirin'! Of course, the facts are that, while in the treatment of susceptible conditions the symptomatic relief is spectacular, the results are in most cases transitory and symptoms return with cessation of therapy. The dangers of undesirable side-reactions at therapeutic levels of dosage are very real. In diseases not susceptible to symptomatic relief the results of administration of cortisone may be not merely negative, but downright dangerous. For example, the administration of cortisone in pulmonary tuberculosis is likely to cause exacerbation of the disease.

In the treatment of rheumatoid arthritis, where the most spectacular success with cortisone has been achieved, in the relief of otherwise intractable and progressive symptoms, energies have been concentrated on working out regimes in which an attempt is made to secure a nice balance between continuous symptomatic relief and the avoidance of onset of undesired and troublesome side reactions. Current clinical

studies in the U.S.A. indicate the desirability of an initial large rate of dosage to suppress the symptoms of rheumatoid arthritis. This may range from 30-200 mg. cortisone acetate daily for from two to three weeks. Approximately one-third of the patients display supression by a daily dose of 75 mg. or less and 20 per cent by a daily dose of 50 mg. or less. The maintenance dose is then established by a daily decrement in dosage to a figure which gives reasonable balance between symptoms and side-effects. Approximately 86 per cent of the patients are maintained at 75 mg. or less daily and more than 50 per cent by 50 mg. or less daily. Undesirable symptoms may include rounding of the face ('moon-face'), development of striae, hirsutism and pigmentation of the skin, psychic changes (usually in unstable subjects); blood pressure increase, aggravation of kidney dysfunction if present, aggravation of diabetic condition if present, delay in wound-healing, the possibility of perforation of peptic ulcer or in appendicitis with consequent acute peritonitis, the exacerbation of systemic infection and so on.

Cortisone Side-Reactions

Boland (*Brit. Med. J.*, 1951, No. 4,725, 191) refers to a group of rheumatoid arthritis patients who were enabled to receive maintenance doses of cortisone continuously for from six to fifteen months. Hormonal excess developed in 40 per cent of the patients such as to necessitate reduction of cortisone dosage with the inevitable reduced efficacy of the therapy. The side-reactions he mentions include disturbances in fat, carbohydrate, protein and electrolyte metabolism and, also, cutaneous, skeletal and psychic changes. He found suppression of adrenal cortical activity during the period of cortisone administration but in most cases this returned to normal after therapy ceased.

Present thinking is—contrary to earlier hopes and expectations by the layman—that, in most instances, the administration of cortisone is to be regarded as a life-saving measure in the acute phases of such diseases as are capable of being brought into remission. Boland (*vide supra*) considers that the treatment of rheumatoid arthritics is attended with distinct limitations, difficulties and dangers and that it is not the treatment of choice in most cases.

Kendall, in his oration delivered to the Heberden Society in London in September (*Brit. Med. J.*, 1951, No. 4,743, 1295), suggests that, from available evidence accumulated especially since he and Hench announced the dramatic effect of cortisone on the symptoms of rheumatoid arthritis, the disease is not of bacterial causation, nor is it a metabolic disease caused by the disturbance of the endocrine glands. He believes that other fields must be searched for the causation of the disease and especially those referring to the states of hyposensitivity and the various phenomena associated with allergens, antigens, and antibodies. He observes that cortisone can modify the effects of large numbers of chemical irritants and protein antigens and suggests consideration of the possibility that rheumatoid arthritis may be due to the intervention of such substances against which cortisone can give protection.

Bjorneboe (*Nordisk. Medicin*, 1951, *45*, 383; through *J. Amer. Med. Ass.*, 1951, *146* (13), 126) thinks along similar lines. He reviews the experiments on the effects of cortisone and ACTH on the concentration of antibodies circulating in the blood and proposes the hypothesis that, in diseases where antibody formation is injurious, substances that inhibit antibody formation (adrenocortical hormones) will be effective. In diseases where prognesis clearly depends upon the ability of the organism to form antibodies, adrenocortical hormones will be ineffective.

Wound-healing Delayed

That the administration of cortisone delays the healing of wounds—whether due to accident or surgical intervention—is now well-established. More recent investigations have established the danger of cortisone administration in the presence of tubercular infection. Lurie showed by animal experimentation that the progress of the disease was greatly accelerated by the administration of cortisone to experimentally infected animals. During the past twelve months evidence has accumulated that prognosis is similarly unfavourable in the case of human beings. Experience in this connection is, at present, scattered and the American Trudean Society is seeking to collate data in the matter (*J. Amer. Med. Ass.*, 1951, *147* (3), 275). Lellaestre (*J. Clin. Invest.*, 1951, *30*, 435) found that when cortisone was administered to patients with far-advanced pulmonary tuberculosis, there was a temporary feeling of well-being, increased strength, defer-

vescence and other advantageous features; but these favourable conditions could not be maintained and, after the cessation of cortisone therapy, the symptoms returned equal to, or worse than, those experienced before administration of the drug.

However, until wider experience is gained the issue still remains somewhat equivocal; but, in the meantime, it is generally considered that the administration of cortisone to tubercular patients must be treated with great caution.

The effect of cortisone on the course of a wide range of human afflictions has come under consideration during the past two years. Its great effectiveness in the relief of various rheumatic complaints is well-known. It has been pointed out that its use in some complaints—such as pulmonary tuberculosis and peptic ulcer—is attended with danger. In some instances the results of treatment with cortisone are without effect one way or another. For example, Criell *et al.* (*J. Amer. Med. Ass.*, 1950, *147*, 1279) have shown by careful statistical analysis of clinical and biochemical data that cortisone has neither a beneficial nor a deleterious effect in poliomyelitis.

Salicylates Stimulate Adrenal Cortex

It has been realised for some time that cortisone and salicylates have a somewhat similar qualitative effect on the course of a number of rheumatic conditions. From these circumstances has arisen the popular impression that cortisone is a sort of 'glorified aspirin'. Salicylates and acetylsalicylates are well-established as the drugs of choice in the treatment of rheumatic conditions, as has been shown by the pioneering work of Coburn and other workers in the field. The effects of salicylates or acetylsalicylate on urinary excretion of ketosteroids, on the number of circulating eosinophils (white blood corpuscles stainable by eosin), in depleting the ascorbic acid content in the adrenal gland, in enhancing the urinary excretion of uric acid, in the inhibition of hyaluronidase (the spreading factor), in symptomatic relief of rheumatic conditions, resemble so closely those of cortisone and ACTH—qualitatively, at least—that there is good reason to believe that salicylates and acetylsalicylates stimulate the adrenal cortex to secrete cortisone and other steroids by direct or indirect routes.

Attention has naturally turned to the hitherto obscure mode of action of salicylates in the light of the new knowledge gained through the study of cortisone and ACTH. Following his earlier work on urinary excretion of adrenocortical steroids during intensive salicylate therapy, van Cauwenberge (*Lancet*, 1951, ii, 374) has given consideration as to whether or not salicylates exert their effects directly upon the cortex of the adrenal gland, or *via* the hypothalamus and the pituitary gland. From his experiments he concludes that the action on the adrenal cortex is *indirect* through the pituitary axis. Later (*Lancet*, 1951, ii, 686) the same author reports the specificity of the salicyl radicle in this connection.

Superiority not yet Demonstrated

The general feeling is that the superiority of ACTH treatment over that by salicylates in the treatment of rheumatic fever has yet to be demonstrated and a series of clinical trials by Bywaters is to be undertaken to clarify this point (*Brit. Med. J.*, 1951, No. 4734, 785). As is well known, the principle risk in rheumatic fever is the possibility of involvement of and permanent damage to the heart and this is the criterion by which, it is suggested, the merits of ACTH treatment as compared by that with salicylates must be finally judged.

The apparent similarity of action between salicylates and cortisone has also led Hetzel and Hine (*Lancet*, 1951, ii, 74) to investigate the effects of salicylate on the pituitary and suprarenal glands. These workers investigated the effect of sodium salicylate, sodium *p*-aminosalicylate and calcium acetylsalicylate (in the soluble, stable form of 'Disprin'). They found that, in rats, therapeutic doses of salicylate caused significant depletion of ascorbic acid in the adrenal glands. The effect could be inhibited by hypophysectomy (excision of the pituitary gland) and tended to be inhibited by preliminary treatment with suprarenal cortical hormone. These facts seem to indicate that the effects of salicylate and acetylsalicylate are mediated by the suprarenal glands and pituitary gland. There appeared to be little, if any, difference between the effects of salicylate (administered as sodium salicylate) and acetylsalicylate (administered as 'Disprin')

Meade and Smith (*Lancet*, 1951ﬁ ii, 224) point out that the work of Hetzel and Hine supports similar conclusions drawn from

their own investigations on the administration of salicylates to guinea-pigs in which they were able to demonstrate an eosinperia (deficiency of eosinphil cells in the blood) and an increase in excretion of 17-ketosteroids. However, these authors point out that the parallelism between the action of cortisone and ACTH, on the one hand, and salicylates, on the other hand, breaks down in other connections. For example: (a) aspirin caused a lessening in glycosuria in mildly diabetic rats, whereas cortisone exacerbated the condition; (b) salicylates increase blood clotting time in man, whereas cortisone and ACTH have been observed to decrease it; (c) cortisone inhibits formation of granulation tissue and wound healing, whereas salicylates do not do so.

Future Unforeseen

It is clear that the continuing comparative pharmacological and biochemical studies between cortisone and the humble aspirin may open up a new field of knowledge of bodily mechanisms and there is no forecasting to what this may lead.

Cortisone still remains scarce even in America where the shortage is described by Boland as severe (*Brit. Med. J.*, 1951, No. 4725, 191). This situation exists despite the enormous effort being directed towards production. Merck production of cortisone is reported now to be enough to treat 90,000 rheumatoid arthritis patients per annum. This is, however, only a small fraction of the sufferers from this complaint in the U.S.A. alone. Merck are understood to expect to be able to double their output of this synthetic in 1952. In the meantime, the cost of cortisone has been reduced from the initial price of $200.00 per gram in 1949 to $16.50 per gram in 1951—all at wholesale prices. The manufacturers are also reported (*Dr. & Cos. Ind.*, 1951, *69* (3), 306; 309) now to be employing four naturally occurring steroids for the synthesis—yeast ergosterol, diosgenin, the glycoside from the Mexican yarn, soya bean stigmasterol, and cholesterol from wool fat and spinal column.

Hecogenin from sisal waste is another possible starting material for cortisone synthesis which is being explored by British investigators under the auspices of the Medical Research Council. Hecogenin has been found to be present in sisal waste to the extent of 0.1 per cent. Many tens of thousands of tons of sisal waste are available yearly in E. Africa.

Because of the scarcity of cortisone attention has been directed to the possibility of economising its use by some synergistic combination or by the sparing action of other drugs simultaneously administered.

Henderson *et al.* (*J. Clin. Endocrinol*, 1950, *10*, 800) administered insulin simultaneously with cortisone and claimed that by so doing, the maintenance dose of cortisone in rheumatoid arthritis could be decreased with the simultaneous reduction of risk of untoward reaction.

Wiesel *et al.* (*Amer. J. Med. Sc.*, 1951, *272*, 243) suggest that an analogy may be drawn between the œstrogenic steriods and cortisone. Oestrogens are known to be inactivated by the liver and this inactivation is antagonised by *p*-aminobenzoic acid. Cortisone is also inactivated within the body at an unknown site. It seemed likely to these workers that *p*-aminobenzoic acid might antagonise such inactivation. Experiments confirmed this seeming likelihood. Rheumatoid arthritics were maintained in remission by as little as 25 mg. cortisone daily provided 12 gram *p*-aminobenzoic acid was similarly administered daily. These observations suggest the liver as the possible site of inactivation of cortisone and would suggest that oral cortisone would be less effective than parenteral cortisone because, on oral administration, it would be presumed to be passed to the peripheral site of action by the portal blood circulation after absorption through the intestine and *via* the liver.

Mode of Action in Doubt

However, it has to be remembered that *p*-aminobenzoic acid, itself, has been reported to have a modicum of antirheumatic effect and it cannot be ruled out that, in the experiments in question, cortisone *may* have potentiated the antirheumatic action of *p*-aminobenzoic acid. These experiments again raise the problem of the mode of action of salicylates. Is their action due wholly or in part to the prevention or inactivation of adrenocorticosteriods by the liver instead of, or as well as, to the stimulation of corticosteroid secretion by the adrenal gland *via* the pituitary gland, a possibility already commented upon above?

(To be continued)

· PERSONAL ·

MR. HUMPHREY MORLAND was re-elected president of the British Leather Manufacturers' Research Association at its annual general meeting held last month, with MR. HENRY BOOTH, MR. A. W. HUTCHINGS, MR. J. B. SOLOMON and MR. H. WITHINSHAW as vice-presidents. Members of the new council are: MR. H. A. DENSHAM, chairman (re-elected); MR. C. J. PITTARD, vice-chairman; MR. E. A. HUTCHINGS, MR. J. A. ROWLAND, and MR. E. H. CRACK. Two further members, DR. J. R. FURLONG and MR. G. M. HARVEY, were co-opted on to the council.

DR. SAMUEL RAY SCHOLES, Professor of Glass Technology in the New York State College of Ceramics, has been named this year's recipient of the Albert Victor Bleininger Award. The announcement was made recently at a meeting of the Pittsburgh Section of the American Ceramic Society. The award is presented annually in the United States to an outstanding man for 'distinguished achievement in the field of ceramics' and Dr. Scholes is the fifth recipient. The medal and scroll, representing the award, will be presented to him at a dinner to be held in the Hotel Schenley on the evening of 14 March, 1952.

Dr. Scholes has published many technical papers and is author and editor of three books: 'Modern Glass Practice' (1935). 'Glass Tank Furnaces' (translated from French) (1938), and 'Handbook of the Glass Industry' (1941). Since 1937 he has been author of the annual paragraph on glass in the 'Encyclopaedia Britannica Book of the Year'.

MR. BRIAN H. TURPIN, technical and sales director of Quickfit & Quartz, Ltd., manufacturers of industrial and laboratory chemical glassware, of Stone (Staffs.), a member of the Triplex group of companies, who recently returned from a business tour of Holland, Belgium and France, expressed the opinion that technical development in the Low Countries had progressed rapidly and was beginning to compensate for the lost war years.

'These countries offer an excellent market for British industrial and laboratory glassware,' said Mr. Turpin. 'They are eager to bring their scientific and industrial equipment up to date and they want British chemical glassware to help them in this respect.'

MR. S. H. ELLIOTT, who has just returned from an annual business tour of Sweden, Finland, Norway and Denmark is again setting off on a two-months' trip to carry the E-Mil 'flag' to India and Pakistan.

S. H. Elliott

Mr. Elliott travels thousands of miles each year seeking new fields for E-Mil products—the well-known Gold Line and Green Line glassware and thermometers—besides regularly visiting his distributing agents in Canada, Portugal, France, Switzerland, Holland and Belgium. Wherever Mr. Elliott goes he finds competition is keen, but always there is an appreciation of and a continually growing demand for quality products.

The home market benefits appreciably by these many tours because the problems and conditions met with in such varying climates and markets gives a knowledge and experience which can be gained in no other way.

The board of directors of General Metallurgical & Chemical, Ltd., have announced that MR. LESLIE H. COLLINS has been appointed general manager of the company, and that MR. JAMES F. WIDMAN has been appointed a director of the company and manager of the Chemicals Division.

MR. J. M. BROWN, of James M. Brown, Ltd., has recently been elected chairman of the Council of the Zinc Pigment Development Association for 1952-1953. Mr. Brown will be assisted by the two following deputy chairmen:—MR. J. F. E. RUFFELL, of Durham Chemicals, Ltd. (retiring chairman) and MR. H. L. WHITWORTH-JONES, of Imperial Smelting Corporation, Ltd. (chairman-designate).

HOME

Per Ardua ad Astra

Despite shortages of sulphur and other raw materials, exports of chemicals, drugs, dyes, and colours in 1951 reached record figures. Total shipped from the U.K. to the end of October was £118 m., against £87 m. for the same 1950 period. These figures were given at the annual meeting of the Chemical and Allied Trades Section, Manchester Chamber of Commerce, on 3 January. Exports to the U.S. rose from £4 m. to nearly £10 m., and to Canada from £3 m. to £4 m., it was stated.

Petrochemicals, Ltd.

In the article describing the full-scale production of petroleum chemicals at Partington, near Manchester (THE CHEMICAL AGE, **65**, 838-839) the company was referred to as Petroleum Chemicals, Ltd. This should, of course, have been Petrochemicals, Ltd.

Birthday Suggestion

In a New Year message to the 5,000 workers in the large Sheffield engineering and chemical firm of Newton Chambers Ltd., Sir Harold West, managing director, stated: 'What a good thing it would be if we could find some way of stressing the individual in our working life together. Everybody has one thing which is personal and special—a birthday. Can't we have some method in every department or section of remembering birthdays? Everybody at the firm would by that means be remembered and specially thought about on at least one day a year. I hope the thought will be taken up and worked out'.

Export of Isotopes

Great Britain at present leads the world in the export by air of radioactive isotopes, both in the number of consignments and the number of countries supplied. All previous records of production and export of atomic products have been broken by the Atomic Energy Research Establishment at Harwell, according to a Ministry of Supply statement last week. During 1951, 9,000 isotopes were produced, an increase of 50 per cent over the previous year, and twice as many consignments as were flown overseas in 1950.

Change of Address

The Technical Information and Documents Unit of the Department of Scientific and Industrial Research was officially transferred on 7 January to Cunard Building, 15 Regent Street, London, S.W.1. (Telephone WHItehall 9788). Owing to the large collection of documents and other equipment involved the unit will be closed, except for urgent inquiries, until Wednesday next, 16 January.

Radium Commission Report

The origin and work of the Radium Commission are described in a new publication recently issued by H.M. Stationery Office. A chapter of this booklet deals with the Commission's relations with other organisations interested in the use of radium, and contains a handsome tribute to the services of Johnson Matthey & Co., Ltd. This company's experience, it says, in the field of gold, silver and platinum metallurgy were invaluable in the rapid growth of clinical investigation in this field, and its unique knowledge of the rare metals and its skill and experience in the handling of radium have been of very great advantage to the Commission and its centres.

Remarkable Variations

Remarkable variations in the types of synthetic rubber are now in the experimental stage, Sir Clive Baillieu, Dunlop chairman, told the Institution of the Rubber Industry (of which he has been appointed president) at their annual dinner in London on 14 December. So far as the Dunlop Company was concerned, he said, they would continue to co-operate in practical measures to establish the manufacture of synthetic rubber in this country, but, he added, they continued to place the highest importance on the assurance of supplies of natural rubber from Malaya and Indonesia which constituted the lifeline of the rubber industry to-day.

Head Office Moved

The head office of Spencer Chapman & Messel, Ltd., will remove to 45 Park Lane, London, W.1, as from 14 January. Telephone number: Grosvenor 4311.

• OVERSEAS •

Plastic Stops Bullets

A new plastic tough enough to stop a .45 revolver bullet fired at ten yards has been developed by the Libby Owens Ford Glass Company, of Toledo, Ohio, it is reported. The material has a higher impact strength than any other material, resists heat and has good electrical insulation. It is made of fibreglass and an admixed plastic resin, not a new combination, but one which can be supplied ready mixed and is easily moulded or formed into various shapes by the usual methods. The new material, which is called Plaskon Reinforced Alkyd Moulding Compound, is being studied for possible military use. Civilian uses are foreseen in refrigerators, washing machines, electronic devices and some motor-car parts.

Shutdown Averted

Dr. R. M. Dorland, director of research for the Abitibi Power & Paper Co., said recently that a possible shutdown of the company's newsprint mill in Sault Ste. Barie had been averted by the development of a new process for making sulphur dioxide. Dr. Dorland said the International Nickel Co. had developed a roasting process to separate nickel ore from sulphur. The process produced liquid sulphur dioxide and Canadian Industries, Ltd., had developed a new method of purifying this liquid gas.

A new plant was being built at Copper Cliff to produce the gas which would be supplied to the Abitibi mill in huge tanks.

A Cure for Stomach Ulcers?

A new Parke-Davis product called 'Kutrol,' is reported to bring quick relief and eventual cure to patients suffering from stomach ulcers. The product has been under investigation since 1930, when Parke-Davis scientists observed that pregnancy had a favourable influence on duodenal ulcer symptoms. Urine extracts from pregnant women and normal men were found to possess a similar activity, and prolonged investigations on animals and human beings have established that Kutrol (uroenterone) is the factor responsible for the activity. No toxicity, idiosyncrasy or intolerance among humans has been found.

European Ceramic Congress

The third congress of the European Ceramic Association will be held in Paris from 12-17 May, and members of the British Ceramic Society have been invited to attend. Local arrangements are being made by the Confederation de Ceramiques de France which estimates that the cost will be about £40 a head. Further details of arrangements will be issued from France in a few weeks.

Cyanide Poisoning

Dr. K. K. Chen, of Indianapolis, U.S.A., has developed a new treatment for cyanide poisoning with sodium nitrate and sodium thiosulphate, injected intravenously, one after the other. The former is intended to produce methæmoglobin which will remove cyanide ions from tissues by the formation of cyamethæmoglobin; and the sodium thiosulphate converts the remaining cyanide to thiocyanate in the presence of rhodanese. Excellent results have been reported in 29 cases, indicating that the method is effective in reviving people poisoned with hydrocyanic acid, potassium cyanide, or calcium cyanide, even after respiration has stopped.

Canadian Potash

The Western Potash Corporation of Canada reports that tests are under way to determine whether brine recovery is an economical method of extracting potash from a bed at Vera, in Saskatchewan, where a three-year permit to potash rights over a wide area is held. The company is committed to spending $75,000 in the first year covered by the permit, commencing March 1951, and $80,000 each succeeding year. Natural gas from two wells brought in this summer by Bata Petroleums, Ltd., will be used in the experiments, it is announced. A pilot plant is in operation at the discovery well. Water forced down to the potash bed (at a depth of 3,468 feet) must be hot in order to dissolve the mineral, and the gas provides the heat. Material forced up by boiling water is expected to contain about 56 per cent potash and 44 per cent common salt. If the Vera project is successful, it will become the first commercial potash development in Canada.

The Chemist's Bookshelf

CHEMICAL INDICATORS. By O. Tomicek. Translated by A. R. Weir, Butterworths Scientific Publications, London. 1951. Pp. X + 258. Figs. 33. 21s. By post 1s. extra.

This comprehensive monograph is provided for students of chemistry up to advanced level, and for workers in analytical laboratories in industry. There is first of all a general theoretical treatment of indicators in neutralisation (acid-base) analysis from the Arrhenius standpoint. The Brönsted-Lowry approach is also discussed while there is brief mention of the corrections to be applied arising from the Debye-Hückel theory. The theory of colour change in indicators, as proposed by Ostwald and modified by workers who followed him, is described. There follows a chapter on the colorimetric determination of *p*H. Separate chapters then deal with the actual applications of indicators to acid-base titration, with oxidation-reduction systems, and with adsorption and fluorescent indicators. A final short chapter discusses a number of otherwise unclassified reagents, such as iodimetric and precipitation indicators. Rather unexpectedly, indicators such as potassium chromate (in Mohr's method) are included under adsorption indicators.

The treatment everywhere assumes little or no previous knowledge on the part of the reader, and proceeds from quite elementary considerations to the point where a number of worked examples of the types of calculations involved are presented. As a consequence, no one in search of information about indicators should be deterred from using the book by the fear that such a specialised book is bound to be difficult.

Of the 37 tables included, almost half are valuable collected lists of indicators, many of them not at all well-known, with data regarding their properties and uses. Each of the chapters dealing with applications is well documented with literature references and there are very full author and subject indexes.

Consideration of the theoretical side of the book leaves the reader most unsatisfied, but this is not necessarily the fault of the author. There is the feeling that the information here presented differs very little from that which was presented to any student of the subject twenty years ago. This would be all right if theories of indicators and titrations were satisfactory, but this is far from being the case. The reader must be struck repeatedly with the way in which the author finds it necessary to qualify his presentation of theoretical principles by the statement that these are only applicable to limited cases. Little guidance is given in the relative advantages and disadvantages of the Brönsted-Lowry theory as opposed to the Arrhenius approach. Altogether one feels that much benefit would have been derived had the author seen fit to attempt to produce an original approach which made more use of modern knowledge of the structure of matter, rather than merely interpreting the classical theories, which are admittedly unsatisfactory.

From the practical point of view a very considerable amount of scattered information, much of it not hitherto readily available to the general worker, has been collected together. This is beyond question the most valuable part of the book. It will undoubtedly, therefore, find much use among analytical chemists, either practising or in the making.—C.L.W.

New Etching Formula

A young etching expert in South Australia has discovered a formula for etching on stainless steel. It is a secret process for the present. Samples of the work have been sent to the United States of America where the inventor is hopeful of finding a market for the formula. His discovery arose out of a request by a friend for a black etching to be made on a stainless steel X-ray component, and it was only after working on the formulae for two years that he finally hit on one which proved to be effective.

Publications & Announcements

A FLUORESCENT microscopy lamp has recently been produced by Hanovia, Ltd., of Slough, Bucks., for the fluorescent analysis of substances under the microscope. Beyond the use of the best available microscope, say the company, no further equipment is required. Contrary to what has too often been said, quartz microscope slides, objectives and condensers are not required, as the ultra-violet wavelength used is 3,660 Å, to which practically all colourless glasses are transparent. The source is a U-shaped quartz arc tube with only 20 mm. between electrodes and 26 mm. in arc length; 80 watts in input energy are consumed to produce the intense brilliance of the mercury arc at a pressure of several atmospheres. The arc tube operates within a ventilated metal hood, mounted to facilitate direction of the rays, which are reduced, by an internal aperture disc, to a narrow beam. This can be focused by the condenser lens and reduced as required by means of the iris diaphragm.

* * *

THE Industrial Group of Philips Electrical, Ltd., have recently produced an illustrated booklet which shows examples of the help they have given to various branches of industry, and outlines the ways in which they can aid modern industry with more economical and efficient methods of production. The booklet shows examples of the way their equipment is used in large and small factories throughout Britain. Photographs illustrate such features as arc welding, combined shrink fitting and hardening by high-frequency heating, and the production assembly gluing of furniture by dielectric loss heating generator.

One of the chapters deals with the new Philips Industrial Application Showroom, which is the central link of a team of design, research and production engineers housed in the same building. Other chapters illustrate the range of Philips electronic measuring instruments, arc welding, resistance welding, etc. Requests for the booklet should be addressed to The Industrial Group, Philips Electrical, Ltd., Century House, Shaftesbury Avenue, London, W.C.2.

* * *

THE September issue of the Mining and Geological Journal, published half-yearly by the Government of Victoria, Australia, is now available. The issue is a centenary one, and contains interesting surveys of a century of progress in the State of Victoria. An interesting article on the gold mining industry from its earliest days tells of first methods of winning the gold and the excitement of the gold rush days. Geological work and its future are also surveyed, as well as the history and prospects of black and brown coal in Victoria, and of oil. The issue includes a review of metals and minerals produced in Victoria.

* * *

THE Transactions of the Indian Institute of Chemical Engineers, Volume III, covering 1949-50, has recently been published. It contains, among other interesting articles, extracts from the presidential address at the Third Annual General Meeting, in which Professor H. L. Roy surveyed the reasons for the lack of chemical engineers in India and the scope that exists for them. Only about 100 chemical engineers graduate each year from Indian institutions, and the country is not yet industrialised enough to put even this small number to good use. Subjects of papers include 'Liquid Fuels', 'The Acceleration of Solar Evaporation by Dyes', 'A Sodium Amalgam Spray Reactor for Dithionite Production' and others.

* * *

A REVIEW of the problems of engineering training is given in a monograph entitled 'Selection, Training and Education for Technical, Supervisory and Managerial Staffs in the Engineering Industry', published by The British Engineers' Association. This interesting monograph warrants study by every firm in the engineering industry. It incorporates a special section dealing with those training problems which particularly affect the smaller firms, filling a gap which has long existed. The appendices include a training schedule for technicians; typical forms for reports and records; an organisation chart for a smaller firm; a list of bodies connected with education and training for industry, and a short bibliography of the important reports impinging on these problems. Copies of the publication are obtainable from the British Engineers' Association, 32 Victoria Street, London, S.W.1, at 2s. each, post paid.

Next Week's Events

MONDAY 14 JANUARY

Society of Chemical Industry

Huddersfield: Technical College, 7 p.m. Dr. W. Cule Davies: 'Polarographic Analysis'.

Institute of Packaging

Manchester: Grand Hotel, 6.30 p.m. Dr. F. W. Clulow (Manchester College of Technology): 'Some Fundamental Considerations in Printing Applied to Packaging'.

TUESDAY 15 JANUARY

Chemical Engineering Group (SCI)

London: Burlington House, Piccadilly, W.1, 5.30 p.m. Norman Brown: 'The Patent Act of 1949'.

Institute of Petroleum

Manchester: Engineers' Club, Albert Square, 6.30 p.m. Annual general meeting. V. M. Farrant: 'Technology and the Salesman'.

Institute of Fuel

London: Institution of Mechanical Engineers, Storey's Gate, St. James's Park, S.W.1, 5.30 p.m. R. B Southall. 'Llandarcy and Fuel Efficiency'.

Institute of Metals

Oxford: 7.0 p.m. Dr. U. R. Evans: 'Corrosion of Metals'.

WEDNESDAY 16 JANUARY

Society of Chemical Industry

London: Waldorf Hotel, Aldwych, W.C.2, 6.30 p.m. Joint meeting with the London & South-Eastern Counties Section, Royal Institute of Chemistry. Professor Kathleen Lonsdale: 'Recent Research in Chemical Crystallography'.

The Chemical Society

Dublin: Trinity College, 7.45 p.m. Dr. F. J. Coll: 'Recent Advances in the Chemistry of Algal Polysaccharides'.

OCCA (London Section)

London: 26 Portland Place, W.1. 7 p.m. F. Armitage, E. F. J. Fry and S. Kut: 'Styrene Polymers—Recent Work on the Course of the Reaction'.

Royal Statistical Society

London: London School of Hygiene and Tropical Medicine, Keppel Street, W.C.1, 5.15 p.m. Research Section. K. D. Tocher: 'The Design and Analysis of Block Experiments'.

Newcastle-on-Tyne: King's College, 7.0 p.m. Industrial Applications Section. North-Eastern Group. Joint meeting with SCI. G.E.P. Box (Imperial Chemical Industries, Ltd.): 'The Rational Design of Experiments'.

THURSDAY 17 JANUARY

The Chemical Society

Dundee: University College, 5.15 p.m. Professor M. Stacey: 'Organic Fluorine Compounds'.

Edinburgh: North British Station Hotel, 7.30 p.m. Joint meeting with RIC and SCI. Lecture and demonstration by Quickfit & Quartz, Ltd.

Manchester: College of Technology, 6.30 p.m. Reading of Original Papers.

Incorporated Plant Engineers

Liverpool: Radiant House, Bold Street, 7.15 p.m. Pilkington Brothers, Ltd., film and demonstration: 'The Processing and Uses of Armourplate and Toughened Glass'

FRIDAY 18 JANUARY

Society of Chemical Industry

London: King's College, Strand, W.C.2, 7 p.m. Fine Chemicals Group. Dr. G. H. Visser (Koniplijke Shell Laboratorium, Amsterdam): 'Fine Chemicals and the Petroleum Industry'.

Institution of Chemical Engineers

Manchester: Town Hall, 2.30 p.m. Reception by Lord Mayor of Manchester followed by annual general meeting, 2.55 p.m. Paper by L. P. O'Brien: 'The British Chemical Industry—A Miscellany after Fifty Years' Service', 4.15 p.m. Tea as guests of the Lord Mayor and Corporation of Manchester. 7 p.m. Midland Hotel. Reception by G. Brearley, chairman of the North Western Branch and L. P. O'Brien, president ABCM. 7.30. Dinner and dance.

London: Caxton Hall, Westminster, S.W.1, 6.30 p.m. Graduates' and Students' Section. D. I. W. Atkinson (Associate Member): 'Management'.

The Chemical Society

Aberdeen: Marischal College, 7.30 p.m. Joint meeting with RIC and SCI. Dr. T. F. Macrae: 'Recent Developments in Vitamin B_{12}'.

Glasgow: University, 7.15 p.m. Tilden Lecture. Professor C. A. Coulson: 'The Contributions of Wave Mechanics to Chemistry'.

Students & Industry

NEED for a higher proportion of high-grade technologists to the number of pure scientists was emphasised by Professor R. S. Hutton in his address to the annual congress of the National Union of Students held at Nottingham University on Monday, 31 December.

In this country, said the professor, there was half a technologist to every pure scientist, whereas in other countries there were 15. He urged that students should be given more opportunity of learning to use libraries and that they should be trained to express technical matters in language that non-technical people could understand.

Grading in industry, Professor Hutton considered, should be better defined. At present there was not sufficient differentiation between the technologist and the technician.

A short course to prepare students for industry was proposed by the speaker, who suggested that this should come immediately after graduation, last preferably one year, but if necessary the length of one vacation.

Market Reports

LONDON.—The demand for industrial chemicals remains steady with new business of moderate dimensions. Reports indicate that buyers are avoiding long-term commitments until the outlook becomes clearer.

Sodium metasilicate is quoted higher at £22 15s. per ton, but otherwise the price position of the soda compounds and of the potash compounds is unchanged, while the movement in these sections is about the average for the period.

As a result of the higher price for linseed oil, the basis price for ground-in-oil white lead and ground-in-oil red lead has been increased by £1 per ton, and the new price for lithopone is £77 per ton.

Coal tar products remain steady with business limited by seasonable influences. Supplies continue on the short side and brisk conditions are expected to return.

MANCHESTER.—Except for textile chemicals, for which the demand is slightly less active, business on the Manchester market during the past week has got back pretty well to the pre-holiday level and steady pressure for deliveries of most descriptions has been reported, especially for the alkalis, and the potash and ammonia compounds. Prices fully maintain their firmness and a fresh general upward movement as a result of the higher cost of coal would not be surprising. There has been rather more business in fertilisers and increasing activity in this section is looked for. The by-products, both light and heavy, are mostly meeting with a brisk demand.

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UNIVERSITY OF LONDON. A Course of Lectures by Professor J. Cathala, arranged for 5.30 p.m. on January 16th, 17th and 18th, at University College, have been postponed.

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Further particulars and forms of application may be obtained from the Office of the **HIGH COMMISSIONER FOR CEYLON IN LONDON, 13, HYDE PARK GARDENS, LONDON, W.2.**

Applications should reach the High Commissioner for Ceylon in London as above on or before twenty-one days from date of this publication.

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ANNOUNCEMENT

ALKALI, ETC., WORKS REGULATION (SCOTLAND) ACT, 1951

NOTICE is hereby given that the Secretary of State proposes to make an Order in exercise of the powers conferred on him by Section 1 of the above Act, to make Orders extending or amending the list of noxious or offensive gases mentioned in Section 27 of the Alkali, etc., Works Regulation Act, 1906, and the list of works mentioned in the First Schedule of that Act, and that an inquiry, as provided for in Sub-sections (1) and (4) of Section 1 of the Act, will be held at St. Andrew's House, Edinburgh 1, at 10.45 a.m., on Friday, 15th February, 1952.

Copies of the draft Order may be obtained on application to the **SECRETARY, DEPARTMENT OF HEALTH FOR SCOTLAND, ST. ANDREW'S HOUSE, EDINBURGH, 1.**

G. MACROBBIE,
Assistant Secretary.

Department of Health for Scotland,
St. Andrew's House,
Edinburgh, 1.

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